

REACTIONS OF AMINE BORANES AND
RELATED COMPOUNDS:
(I) MECHANISM OF DEHYDROGENATION
OF DIMETHYLAMINE BORANE
(II) SYNTHESIS OF TRIMETHYLAMINE
CHLOROBORANES

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PART I. MECHANISM OF DEHYDROGENATION OF DIMETHYLAMINE BORANE

INTRODUCTION

When dimethylamine borane is heated, hydrogen is eliminated and dimethylaminoborane is formed. The mechanism of this reaction should be the same as for the first step in the production of borazenes, for example, N-trimethylborazene, by heating monomethylamine borane. Thus, the reaction mechanism, or molecularity, would be worthy of investigation.

The reaction of dimethylamine borane to yield hydrogen and dimethylaminoborane does not lend itself readily to common methods of kinetic determination such as measuring the increase in total pressure or the concentration of any single species. This is due, in the first case, to such reactions as the dimerization of dimethylaminoborane or the disproportionation of the dimethylaminoborane (7) which occur at significant rates in the temperature range at which hydrogen elimination can be conveniently measured. In the second case, the separation of unreacted dimethylamine borane, or the separation of dimethylaminoborane from the reaction mixture, would be difficult because the reaction would be occurring while the separation was being carried out.

Since conventional kinetic studies were impractical for the most part, the following method was used to yield data which could be used to determine the reaction molecularity. N-deuterodimethylamine borane- d_3 and dimethylamine borane in a 1:1 molar ratio were heated and the non-condensable products analyzed in a mass spectrometer. The ratio of $H_2:HD:D_2$ found was compared to that expected for either a unimolecular or bimolecular reaction. The results indicated a bimolecular reaction and a kinetic isotope effect. The isotope effect was investigated using various isotopic distributions of hydrogen in the dimethylamine borane and analyzing in the mass spectrometer the gaseous products eliminated on heating. The established isotope effect was that hydrogen atoms were eliminated more readily than deuterium atoms.

The possibility of hydrogen-deuterium exchange reactions occurring during the elimination reaction was investigated thoroughly.

EXPERIMENTAL

Nomenclature

The compounds formed by the reaction of an amine and diborane were named as amine adducts of borane. The following is the list of amine boranes in Part (I):

dimethylamine borane, $(\text{CH}_3)_2\text{HNBH}_3$;

dimethylamine borane- d_3 , $(\text{CH}_3)_2\text{HNBD}_3$;

N-deuterodimethylamine borane, $(\text{CH}_3)_2\text{DNBH}_3$;

N-deuterodimethylamine borane- d_3 , $(\text{CH}_3)_2\text{DNBD}_3$.

Origin of reagents

| | |
|-----------------------------------|---------------------------------------|
| D_2O : | Tracerlab, 99.7% D_2O |
| $(\text{CH}_3)_3\text{NBH}_3$: | Callery Chemical Co. |
| $(\text{CH}_3)_2\text{NH}$: | Matheson Co., Inc. |
| SO_2Cl_2 : | Matheson, Coleman and Bell Div. |
| BF_3 : | Matheson Co., Inc. |
| $\text{C}_4\text{H}_9\text{Li}$: | Foote Mineral Co. |
| $(\text{CH}_3)_2\text{HNBH}_3$: | Chemical Procurement Laboratories |
| NaBD_4 : | Alfa-Inorganics |
| LiBH_4 : | Metal Hydrides, Inc. |

Purification of reagents

D_2O used without further purification--being handled in a N_2 atmosphere.

| | |
|---------------------------------|--|
| $(\text{CH}_3)_3\text{NBH}_3$ | sublimed once, then resublimed into the reaction flask (or tube). |
| SO_2Cl_2 | bp 68-70°C, was used without further purification--transferred in a N_2 atmosphere. |
| $(\text{CH}_3)_2\text{NH}$ | stored over Na for over 24 hours in freezer compartment of refrigerator, then distilled into reaction flask (or tube). |
| BF_3 | distilled from a -78° trap through a -119° trap into a -196° trap, then distilled into reaction tube. |
| $\text{C}_4\text{H}_9\text{Li}$ | used without further purification--transferred with a syringe under a flowing stream of N_2 . |
| $(\text{CH}_3)_2\text{HNBH}_3$ | sublimed once, then resublimed into the reaction flask (or tube). |
| $(\text{CH}_3)_3\text{NBD}_3$ | sublimed after preparation and then resublimed into reaction tubes. |
| NaBD_4 | used without further purification. |
| LiBH_4 | used without further purification. |

Instruments

The vacuum system used in the experimental work was similar to the vacuum line described in Synthetic Inorganic Chemistry by W. L. Jolly (21). Apiezon N grease was used on all ground joints in the system.

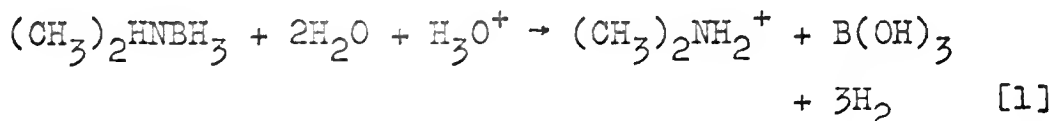
A Bendix Time-of-Flight mass spectrometer was used to obtain the mass spectra.

A Beckman IR-10 or a Perkin-Elmer 21 spectrophotometer was used to obtain the infrared spectra in either the gas phase or in a carbon tetrachloride solution.

General method for the analysis of the dimethylamineboranes

Dimethylamineborane was sublimed from a weighed storage flask into a 50 ml round bottom flask. After the sublimation, the storage flask was weighed, the difference in weight being the amount of sample to be analyzed.

Analysis was based on the equation



The compound was first hydrolyzed by condensing 20 ml of 0.1 N HCl (Acculute) into the flask containing the dimethylamine borane. Hydrolysis was allowed to continue overnight at room temperature. The contents of the reaction flask were condensed in a liquid N₂ bath and the non-condensable gas was transferred into a calibrated bulb by a Toepler pump. The amount of hydrolyzable hydrogen was thus obtained.

The acid solution from the hydrolysis of dimethylamine borane was transferred into a 400 ml, boron-free glass beaker. The boron was determined as boric acid using the mannitol titration method.

The amount of nitrogen, as dimethylammonium ion, could be determined since a known amount of strong acid had been used to hydrolyze the sample. The difference in the equivalents of strong acid added initially and the equiva-

lents of base necessary to neutralize the strong acid remaining after the hydrolysis reaction was the amount of strong acid neutralized by the dimethylamine.

Using this method, the following data in Table 1 were determined.

Pyrolysis of B_2D_6

Diborane- d_6 was pyrolyzed by passing the gas through a 9 mm Vycor tube, 37.5 cm long, surrounded by a 0.75 inch stainless steel pipe and heated by two Meeker burners. The gas was allowed to pass slowly into the tube. Attempts to make more than one pass of material through the hot tube did not increase the amount of non-condensable gas; evidently no condensable material passed through the hot tube. The non-condensable products were Toepler pumped into a flask and analyzed in the mass spectrometer. Results of these experiments were as follows, in Table 2.

TABLE 1
ANALYSIS OF DIMETHYLAMINE BORANES

| Compound | | Per Cent | | \bar{H}^a | Ratio | |
|------------------|------------|----------|-------|-------------|-------|------|
| | | B | N | | B | N |
| $(CH_3)_2DNBD_3$ | calculated | 17.18 | 22.25 | 9.57 | 1.00 | 1.00 |
| | found | 16.56 | 21.47 | 9.08 | 1.00 | 1.00 |
| $(CH_3)_2DNBD_3$ | calculated | 17.18 | 22.25 | 9.57 | 1.00 | 1.00 |
| | found | 17.20 | 22.25 | 9.43 | | |
| $(CH_3)_2HNDB_3$ | calculated | 17.45 | 22.60 | 9.37 | 1.00 | 1.00 |
| | found | 17.48 | 22.70 | 9.65 | | |
| $(CH_3)_2DNBH_3$ | calculated | 18.04 | 23.36 | 5.05 | 1.00 | 1.00 |
| | found | 23.80 | 30.85 | (b) | | |
| $(CH_3)_2HNBH_3$ | calculated | 18.34 | 23.76 | 5.13 | 1.00 | 1.00 |
| | found | 20.23 | 26.08 | 5.51 | | |

^aHydrolyzable.

^bHydrolysis flask leaked.

TABLE 2
PYROLYSIS OF B_2D_6

| Prepared by | B_2D_6 mmoles | Per Cent Reaction | D_2 | Per Cent HD | H_2 |
|--------------------------------|--------------------|----------------------|-------|----------------|-------|
| $(CH_3)_3NBD_3 +$ $BF_3(g)$ | 0.098 | 105.8 | 81.5 | 18.5 | - |
| $NaBD_4 + BF_3(g)$ | 0.12 | 88.9 | 91.0 | 8.4 | 0.5 |

Infrared spectral analysis

The spectra of the dimethylamine boranes (Figures 1, 2, 3, 4, 5) were taken on a Beckman IR-10 spectrophotometer, using matched cells 0.2mm thick and the slow scan speed. The compounds were dissolved in Fischer spectroanalyzed grade carbon tetrachloride and the same solvent was used as a blank in the reference beam. The absorbency, A, expressed as the $\log \frac{\text{Intensity blank}}{\text{Intensity solution}}$ was calculated from the infrared spectra in which transmittancy was plotted as a function of the wave number.

The absorbency of the CH deformation peak at 1475 cm^{-1} was used as the internal reference and all calculations were made with respect to this peak. The results are given in Table 3.

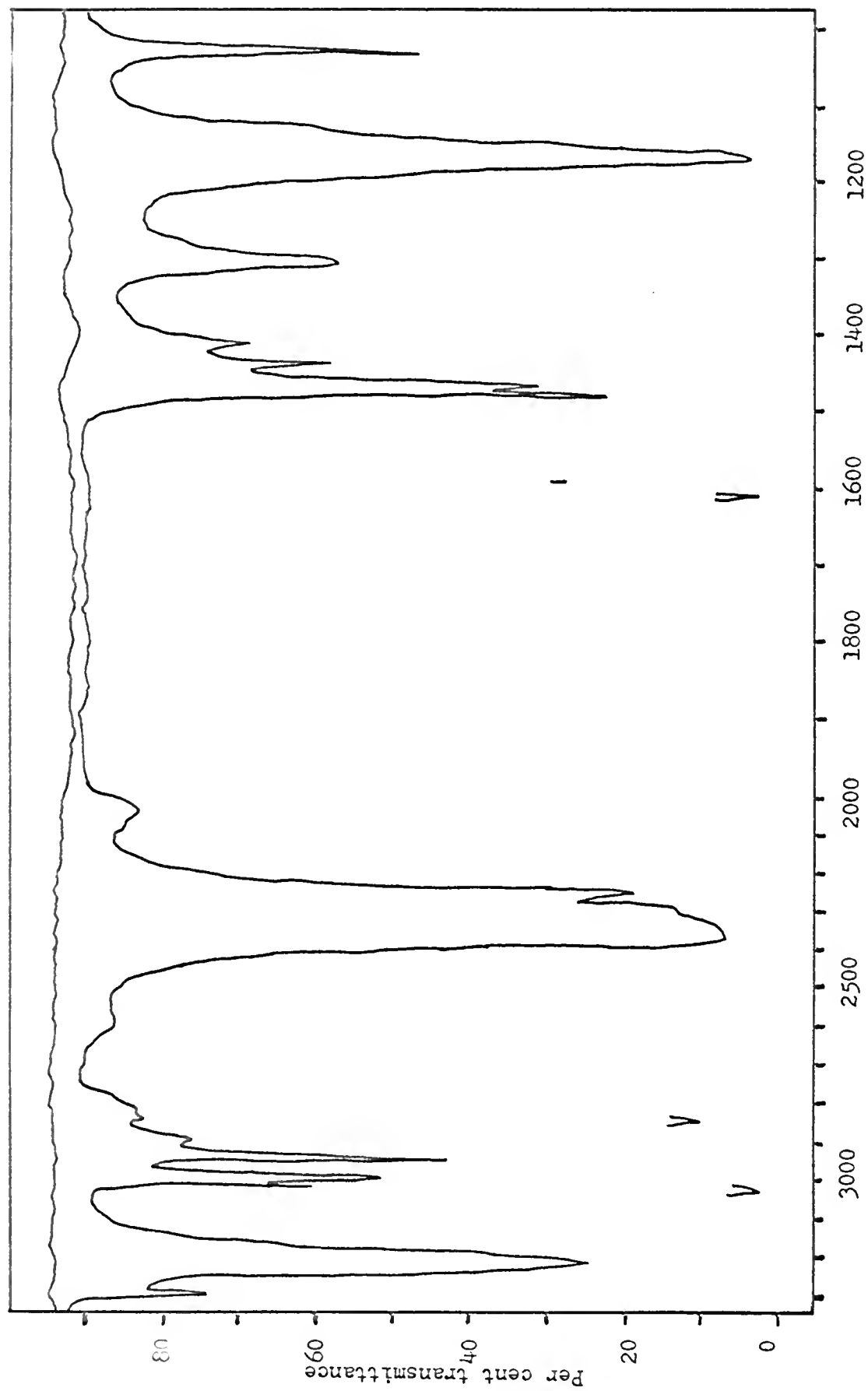


Fig. 1.--Infrared spectrum of $(\text{CH}_3)_2\text{HNBH}_3$.

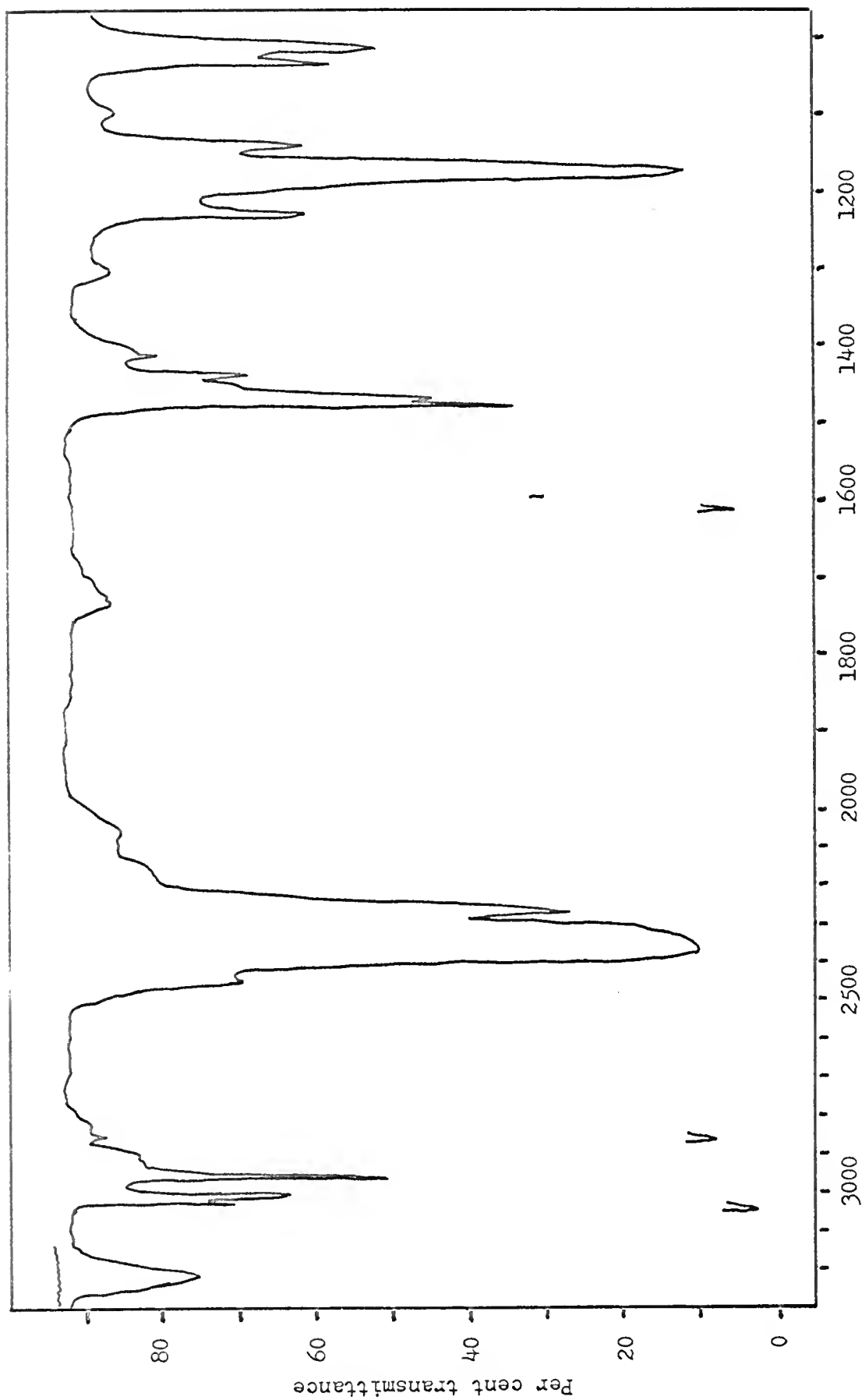


Fig. 2.--Infrared spectrum of $(\text{CH}_3)_2\text{DNEH}_3$.

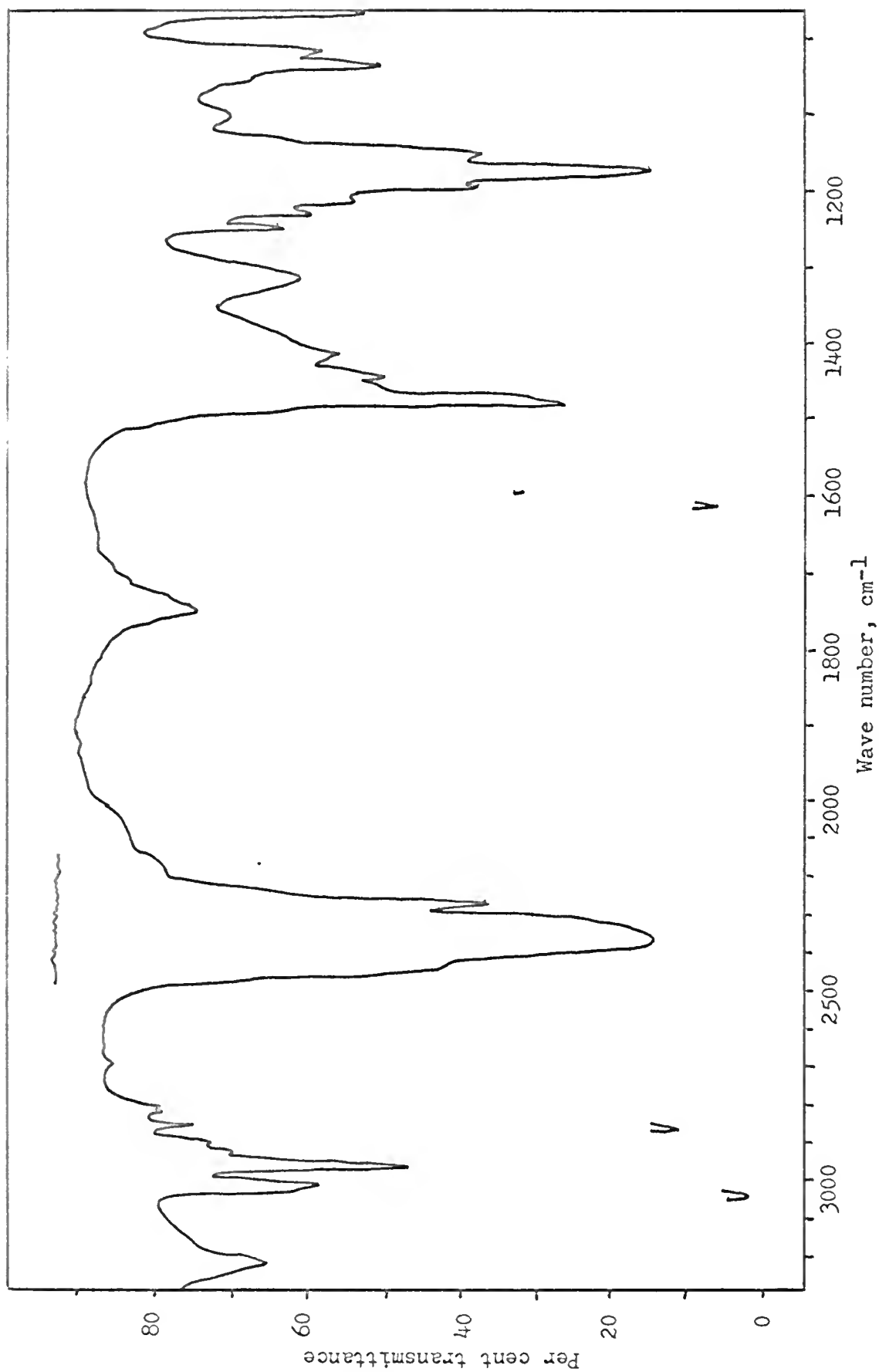


Fig. 3.--Infrared spectrum of $(\text{CH}_3)_2\text{DNBH}_3$ after heating.

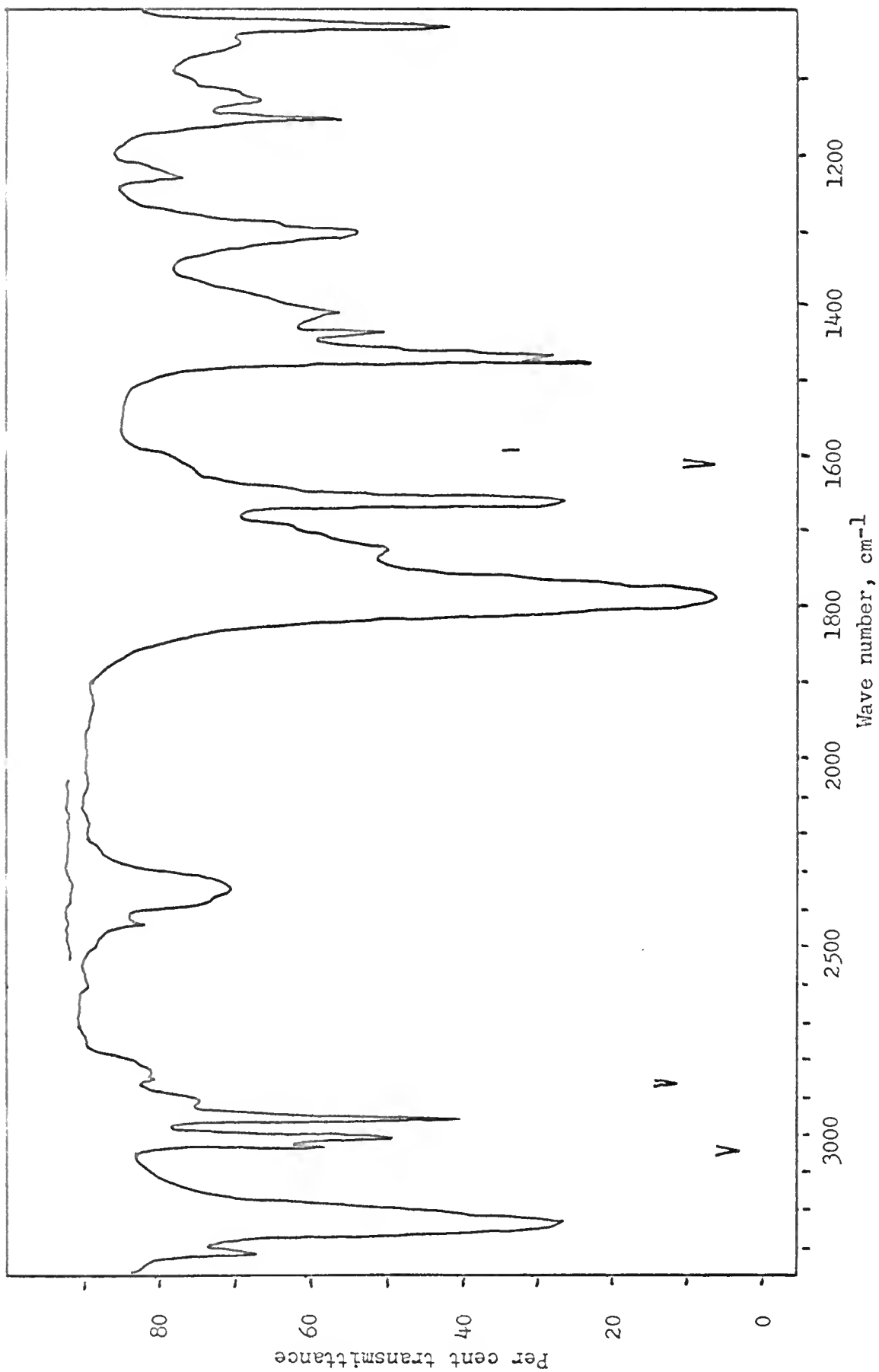


Fig. 4.--Infrared spectrum of $(\text{CH}_3)_2\text{HNBD}_3$.

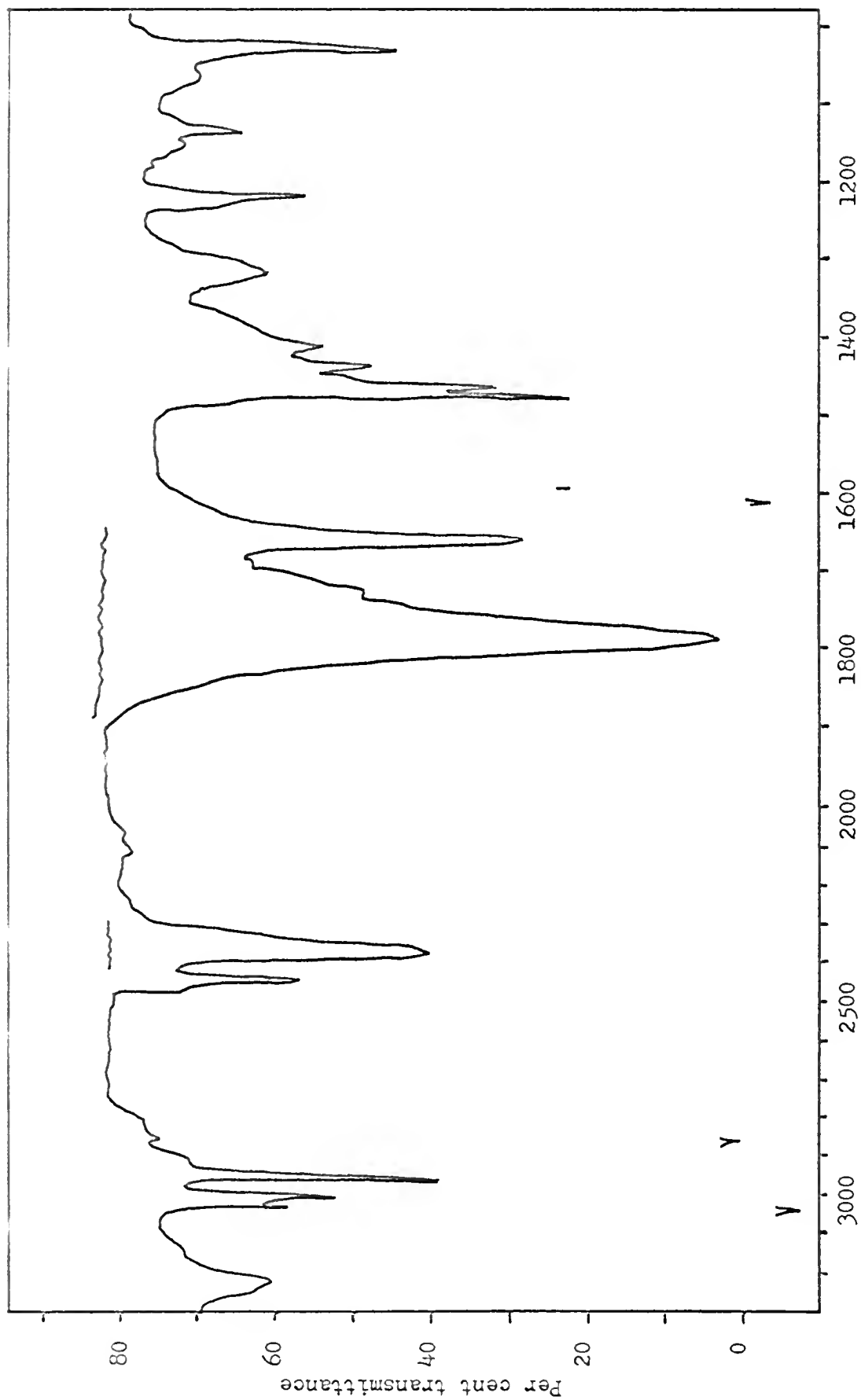


Fig. 5.--Infrared spectrum of (CH₃)₂DNBD3 .

TABLE 3

CALCULATION OF PER CENT DEUTERIUM IN THE DEUTERATED DIMETHYLAMINE BORANES FROM INFRARED SPECTRA USING THE CH DEFORMATION PEAK AS THE INTERNAL REFERENCE

| Compound | Figure | Log $\frac{\text{I blank}}{\text{I solution}}$ | $\frac{A_x}{A_{CH}}$ | Per Cent Relative to CH | Total Per Cent D |
|-------------------|--------|--|----------------------|-------------------------|------------------|
| $(CH_3)_2HNBH_3$ | 7 | | | | |
| NH | | 0.58320 | 0.992 | | |
| BH | | 1.11727 | 1.90 | | |
| CH | | 0.58771 | | | |
| $(CH_3)_2^DNBH_3$ | 2 | | | | 81.1 |
| NH | | 0.09342 | 0.218 | 22.0 | |
| ND | | 0.95904 | 2.240 | 78.0 | |
| BH | | | | 96.9 | |
| BD | | 0.02531 | 0.059 | 3.1 | |
| CH | | 0.42813 | | | |
| $(CH_3)_2^DNBH_3$ | 3 | after heating | | | 93.5 |
| NH | | 0.07918 | 0.148 | 15 | |
| ND | | 0.79865 | 1.50 | 85 | |
| BH | | | | 91.5 | |
| BD | | 0.08636 | 0.162 | 8.5 | |
| CH | | 0.53403 | | | |

Table 3 (cont'd)

| Compound | Figure | Log $\frac{I}{I_{\text{blank}}}$ | $\frac{A_x}{A_{CH}}$ | Per Cent Relative to CH | Total Per Cent D |
|------------------|--------|----------------------------------|----------------------|-------------------------|------------------|
| $(CH_3)_2HNBD_3$ | 4 | | | | 108.4 |
| NH | | 0.56110 | 0.924 | 93 | |
| ND | > | 0.10380 | 0.171 | 7 | |
| BH | | | | 2 | |
| BD | | 1.25042 | 2.06 | 108.4 ^a | |
| CH | | 0.60746 | | | |
| $(CH_3)_2DNBD_3$ | 5 | | | | 189.1 |
| NH | | 0.5690 | 0.126 | 13 | |
| ND | > | 0.26007 | 0.574 | 87 | |
| BH | | | | | |
| BD | | 0.87967 | 1.941 | 102.1 | |
| CH | | 0.45332 | | | |

^aPer cent deuterium would be 100 if only BD bonds and no ND bonds present.

The ratio of the absorptivities of the BH:CH and the NH:CH in the spectrum of the completely undeuterated sample were found to be 1.90 and 0.992, respectively. The per cent NH and ND were calculated as follows:

$$\frac{A_{\text{NH}}}{A_{\text{CH}}} = \frac{a_{\text{NH}}}{a_{\text{CH}}} \frac{C_{\text{NH}}}{C_{\text{CH}}}$$

$A_{\text{NH}}/A_{\text{CH}}$ calculated from spectra

$a_{\text{NH}}/a_{\text{CH}}$ absorptivity ratio from spectrum of undeuterated compound

$C_{\text{NH}}/C_{\text{CH}}$ ratio of concentrations

Assume in partially deuterated compounds that

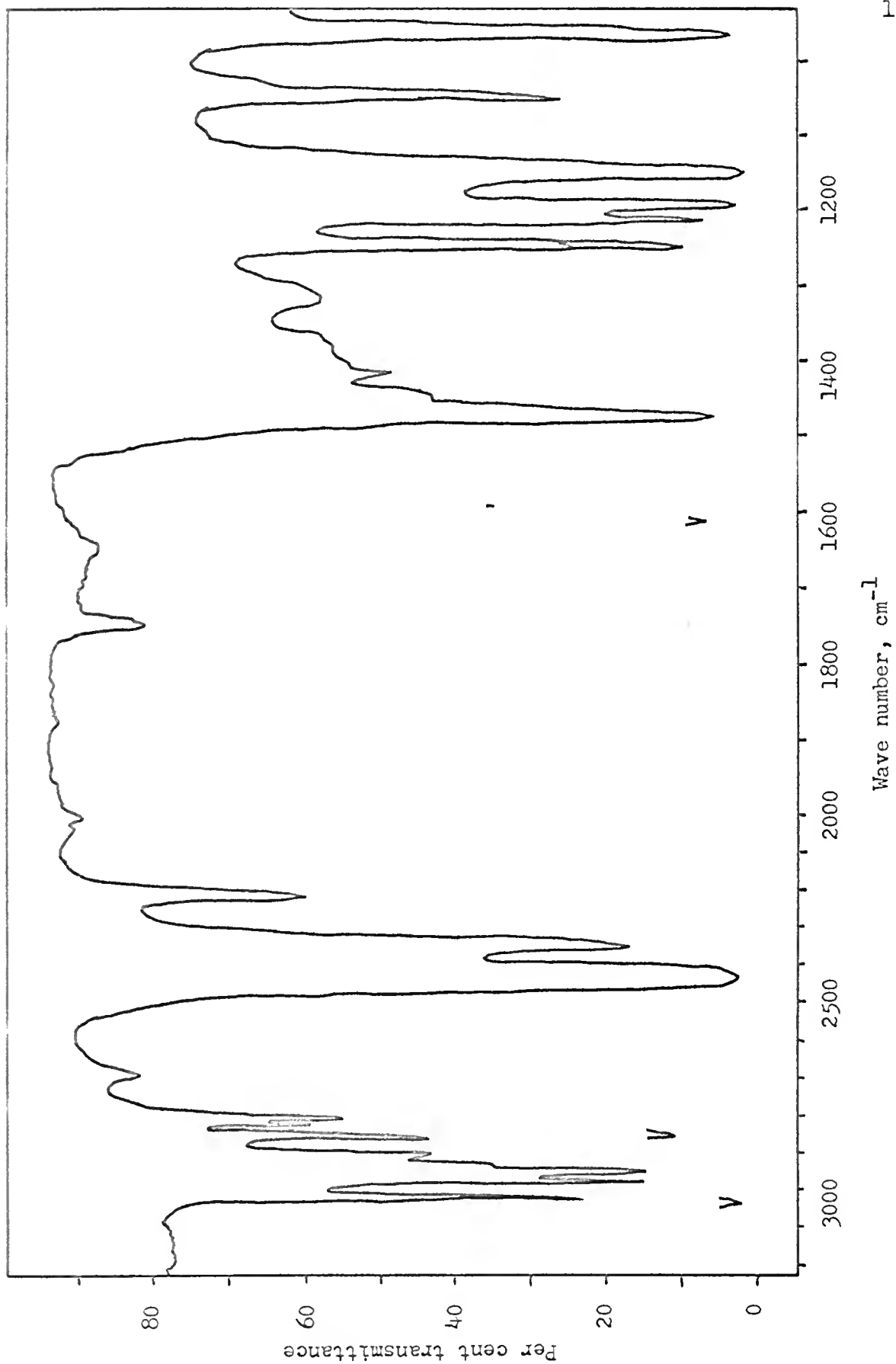
$$C_{\text{NH}} + C_{\text{ND}} = C_{\text{CH}}$$

$$C_{\text{BH}} + C_{\text{BD}} = C_{\text{CH}} \quad .$$

This assumption allowed C_{ND} to be determined without the actual absorbency being known. This was necessary since the ND and BH stretching frequencies both occur between 2300-2500 cm^{-1} . It was not possible to separate the absorbency due to each vibration. Since $(\text{CH}_3)_2\text{DNBD}_3$ was known not to be completely deuterated from mass spectral data of the B_2D_6 pyrolysis product, the absorptivity ratio of BD:CH could not be obtained for its infrared spectrum. Therefore, the ratio of the absorptivities for BD:CH was assumed to be the same as that for BH:CH.

The absorptivity ratio of BH:CH for the volatile reaction product after heating $(\text{CH}_3)_2\text{HNBH}_3$ for thirty-four hours at 100° was 1.30 (Figure 6). Thus, one of the BH containing products which was formed when dimethylamine borane was heated, did not absorb as strongly in the BH stretching vibration region as did the original starting material. This could cause a lower estimation of the amount of BH-containing material after heating than would actually be present and therefore introduce an error in any calculations made using the BH stretching absorption.

The absorption in the $1700\text{--}1800\text{ cm}^{-1}$ region which was attributed to the BD stretching vibration in the molecule $(\text{CH}_3)_2\text{HNBX}_3$ [X=H and/or D] did not occur at exactly the same wave number in each spectra. The absorption varied from 1735 to 1785 cm^{-1} . Qualitatively, this variation appeared to be concentration dependent. The greater the concentration of BD bonds in the molecule the larger the wave number at which the absorption occurred. The absorption for the BD stretching vibration in $(\text{CH}_3)_2\text{DNBD}_3$ occurred at 1785 cm^{-1} and for $(\text{CH}_3)_2\text{DNBH}_3$ containing 3 per cent BD bonds, at 1735 cm^{-1} . An explanation for this variation could be that a shift in the stretching vibration occurred in the -BH_3 group as the hydrogen atoms in the -BH_3 group were replaced by deuterium atoms. The largest shift was implied by the spectra at low D_2 percentages when mostly BH_2D groups should have been present.

Fig. 6.---Infrared spectrum of $(\text{CH}_3)_2\text{HNBH}_3$ after heating.

Mass spectral analysis

A Bendix Time-of-Flight Mass Spectrometer was used for the analysis. The sensitivity coefficient of the spectrometer to H_2 and D_2 was determined before each set of analyses, using commercial samples of hydrogen and deuterium gas. The sensitivity coefficients used in calculating the data were obtained at the same total pressure as that in the sample. In calculating the results of the hydrogen elimination reaction the sensitivity coefficient for HD was assumed to be intermediate between that of H_2 and D_2 . This assumption proved to be a valid one as may be seen by the graphs of pressure versus sensitivity coefficient in Figure 7.

Three sets of sensitivity coefficients were determined and listed in Table 4. A sensitivity coefficient for HD was determined from a gas sample prepared by the hydrolysis of CaH_2 with D_2O . This gas sample contained small amounts of D_2 and H_2 , but it was predominantly HD. The spectra were corrected for the presence of D_2 and H_2 and then the sensitivity coefficient of HD was calculated. The variation in the sensitivity coefficients with total pressure was determined and plotted in Figure 7. In samples containing D_2 , the H_2 content was determined from the peak at m/e 2 after subtracting the portion due to D^+ . The necessary data were obtained from the intensity ratio of m/e 4 and m/e 2 peaks in the mass spectrum of pure D_2 .

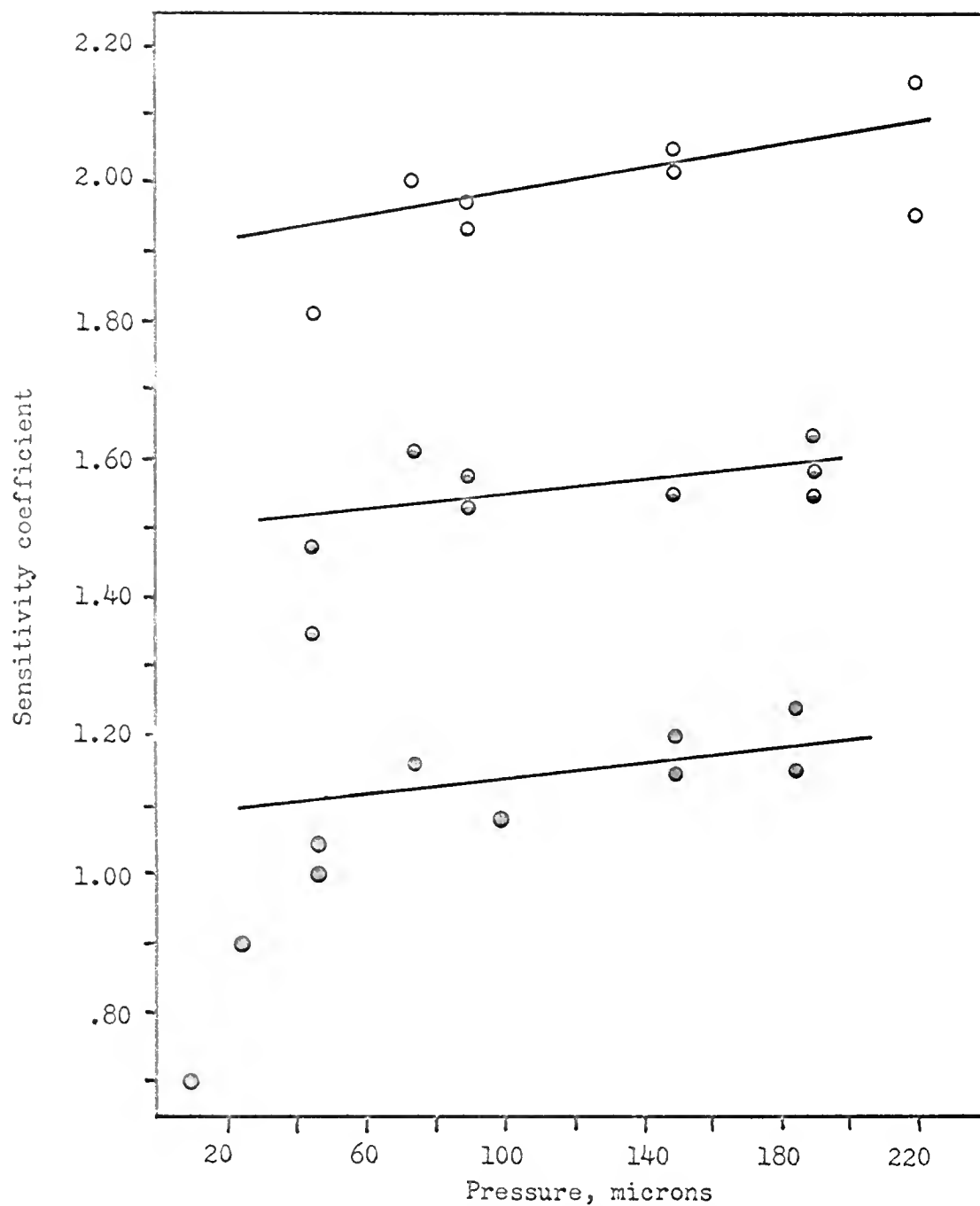


Fig. 7.--Mass spectrometer sensitivity coefficient of H_2 , HD and D_2 as a function of total pressure.
 (○) D_2 ; (◐) HD; (●) H_2 .

TABLE 4

SENSITIVITY COEFFICIENT OF MASS SPECTROMETER FOR H₂, HD AND D₂

| Sensitivity Coefficients ^a | | | Used to Calculate Analysis of: |
|---------------------------------------|----------------------------------|----------------------------------|---|
| H ₂ | HD | D ₂ | |
| 0.532 $\frac{\text{units}}{\mu}$ | 0.561 $\frac{\text{units}}{\mu}$ | 0.590 $\frac{\text{units}}{\mu}$ | (CH ₃) ₂ DNBD + (CH ₃) ₂ HNBH ₃ |
| | | | $\xrightarrow[100^\circ]{24 \text{ hrs}}$ and gas sample from hydrolysis of (CH ₃) ₂ DNBD ₃ |
| 0.733 $\frac{\text{mm}}{\mu}$ | 1.17 $\frac{\text{mm}}{\mu}$ | 1.27 $\frac{\text{mm}}{\mu}$ | All other H ₂ elimination reactions and the amine exchange reactions |

^aFor the values used in the analysis of gases from heating the deuterated amine boranes by themselves see Figure 7.^bCalculated from spectra which were predominantly HD.

The mass spectra of the solid dimethylamineboranes were obtained at 70 ev by placing the sample on the end of a probe which extended into the ionization chamber. The probe was at room temperature during the measurement of the spectra. The vapor pressure of dimethylamineborane at room temperature was sufficient to produce good spectra. For the results of these analyses see Figures 8, 9, 10 and 11.

The mass spectra of the solid compounds showed a low intensity peak at the m/e corresponding to the mass of the parent compound. The mass peak of m/e one less than the parent peak, and the parent peak had a ratio of 8.4 in the cases where the hydrogen was bonded to the boron atom and a deuterium bonded to the nitrogen atom compared to 7.9 for the reverse case where hydrogen was bonded to nitrogen and deuterium to boron. This suggested that the BH bonds were lost more readily than NH bonds. The spectra of the completely deuterated and undeuterated compounds also showed the same trend as indicated in Table 5. The ratio of the m/e peak of mass two less than the parent peak, to the parent peak, implied that a BD bond was lost much more readily than an ND bond.

The most intense m/e peak in each spectrum corresponded to the loss of a deuterium atom when the compound contained BD bonds and to the loss of a hydrogen atom when the compound contained BH bonds. But the numerous peaks, in

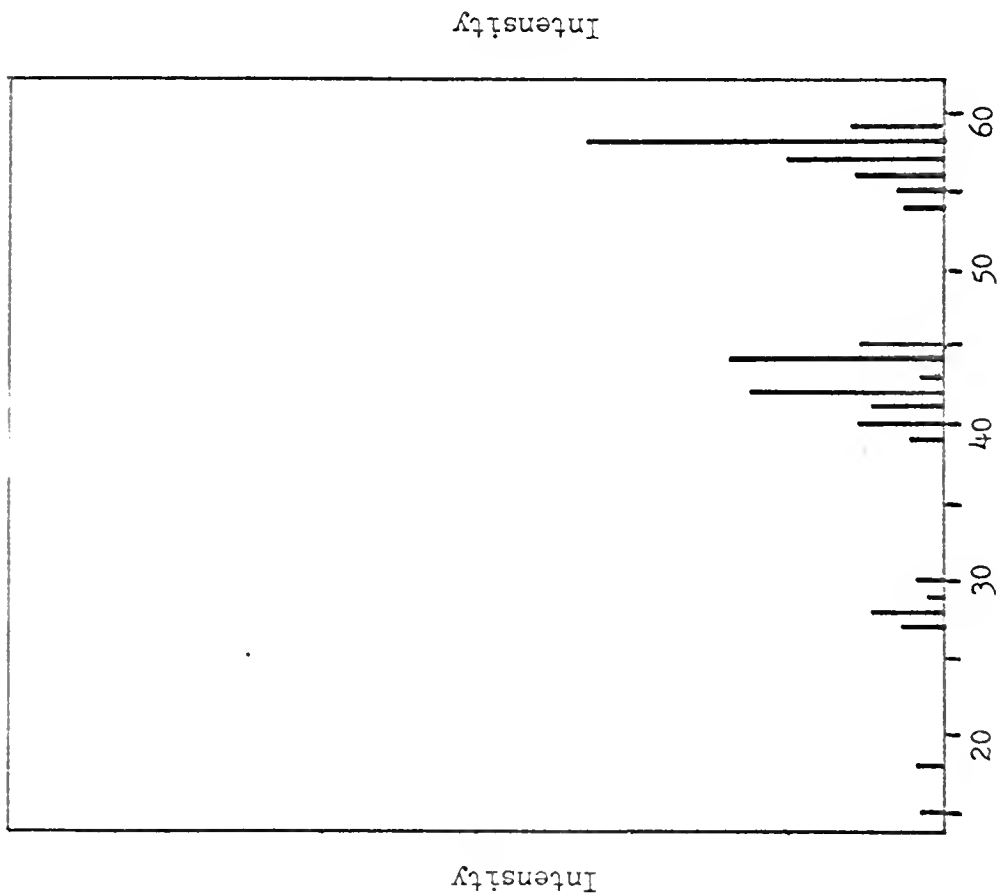


Fig. 8.--Mass spectrum of $(\text{CH}_3)_2\text{HNBH}_3$ at 70 ev.

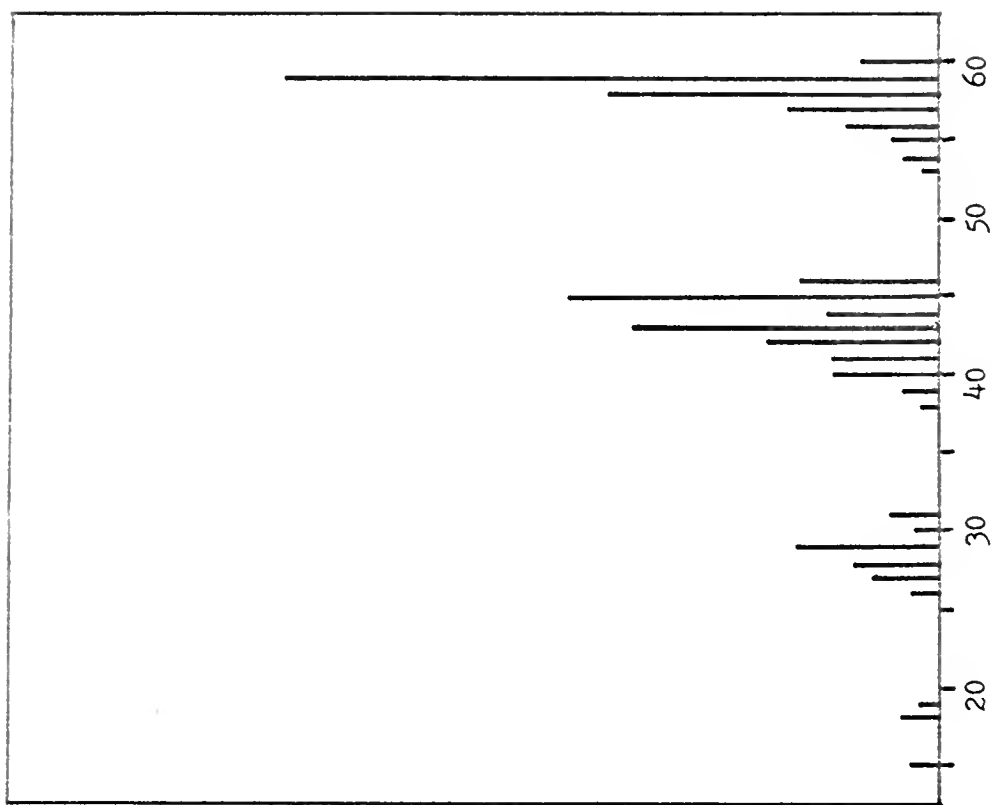


Fig. 9.--Mass spectrum of $(\text{CH}_3)_2\text{DNBH}_3$ at 70 ev.

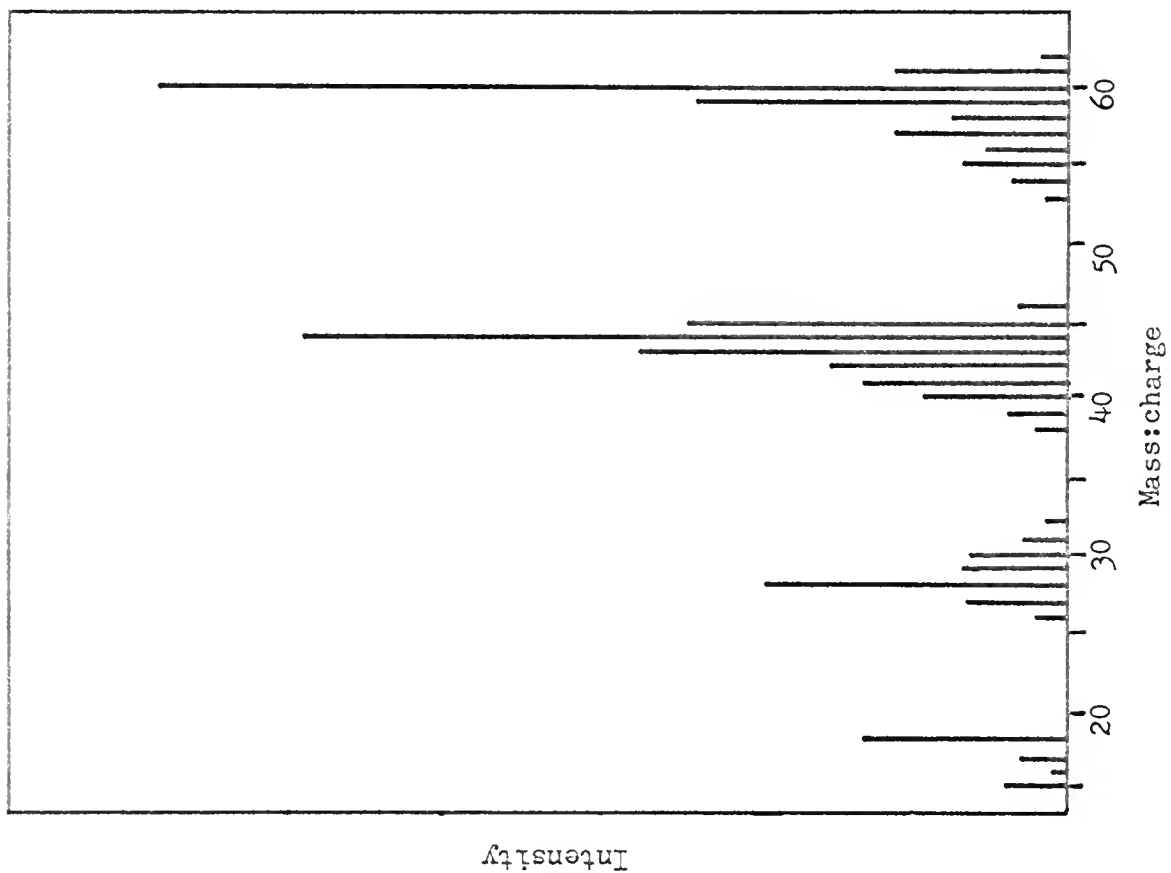


Fig. 10.--Mass spectrum of $(\text{CH}_3)_2\text{HNBD}_3$ at 70 ev.

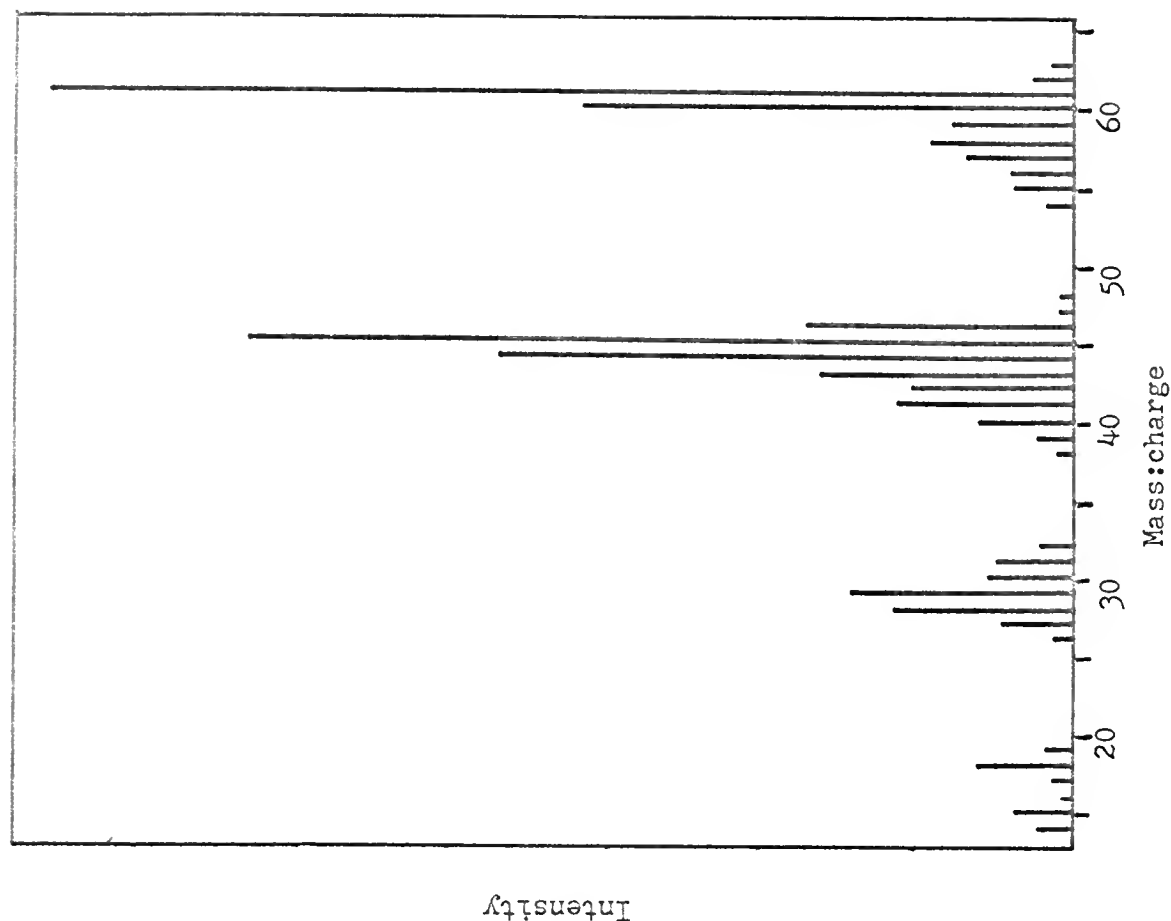


Fig. 11.--Mass spectrum of $(\text{CH}_3)_2\text{DNBD}_3$ at 70 ev.

TABLE 5
TENDENCY FOR PARENT ION TO LOSE A HYDROGEN OR DEUTERIUM ATOM

| Compound | Ratio of Mass Intensities | | |
|--------------------------------|--------------------------------------|-------------------------------------|-----------|
| | M/e ratio loss of deuterium | M/e ratio loss of hydrogen | |
| $(\text{CH}_3)_2\text{DNBD}_3$ | 61:63 | 59.8 | 62:63 2.5 |
| $(\text{CH}_3)_2\text{HNBD}_3$ | 60:62 | 41.4 | 61:62 7.9 |
| $(\text{CH}_3)_2\text{DNBH}_3$ | 58:60 | 4.3 | 59:60 8.4 |
| $(\text{CH}_3)_2\text{HNBH}_3$ | | | 58:59 3.8 |

each group of peaks differing only by one m/e unit, suggested that the CH bonds in the methyl groups were also being broken under the conditions at which the spectra were obtained. This would make any quantitative use of the relative peak intensities open to doubt as to whether the hydrogen atom lost had been originally bonded to a carbon, nitrogen or boron atom.

Preparation of $(\text{CH}_3)_3\text{NBD}_3$ from $(\text{CH}_3)_3\text{NBH}_3$ in an acidic D_2O solution (11)

Sulfuryl chloride (0.5 ml) was pipetted into a flask containing deuterium oxide (20 ml) in a dry nitrogen atmosphere and stirred magnetically for twenty minutes. Trimethylamineborane (13.7 mmoles) was dissolved into 50 ml of anhydrous diethyl ether in a 200 ml round bottom flask. The deuterium oxide solution was poured into the ether solution and immediately the flask was fitted with an adapter for the vacuum system, attached to the system, and submerged in liquid N_2 , and evacuated.

The reaction flask was warmed to room temperature (24°) and stirred magnetically. After six hours, the reaction mixture was condensed in liquid N_2 and, in approximately a 400 ml volume, there was 95.5 mm of non-condensable gas. The D_2O -ether mixture was transferred to a separatory funnel and the reaction flask washed with a 20 ml portion of ether which was then added to the reaction mixture. The

layers were separated, keeping the ether layer in the separatory funnel. Excess anhydrous potassium carbonate was added to the ether solution and the mixture was set aside for forty-five minutes. The ether solution was transferred into a 200 ml round bottom flask, washing the K_2CO_3 with two 20 ml portions of anhydrous ether and the wash solutions added to the ether solution.

The ether was removed by distilling under vacuum from room temperature into a liquid N_2 trap. When liquid ether was no longer visible, a -78° bath was placed about the flask and the last of the ether removed into the liquid N_2 trap. This was to prevent loss of product by sublimation. A white solid residue remained. A white product was sublimed from this residue to give a 74.2 per cent yield.

The infrared spectrum (Figure 12) of the sublimed product in CCl_4 solution agreed with the spectrum of trimethylamineborane with the peaks attributed to a BD stretching vibration shifted to longer wavelengths. There was a peak in the region of the BH stretching vibration, but it was less intense than the BD peak. Assuming the absorptivity coefficient, a , to be the same for both the BD and BH containing compounds, from Beer's law, $A = abc$, the concentration of the BH compound was calculated to be 2.7 per cent of the concentration of the BD compound. No other analyses were made of this compound.

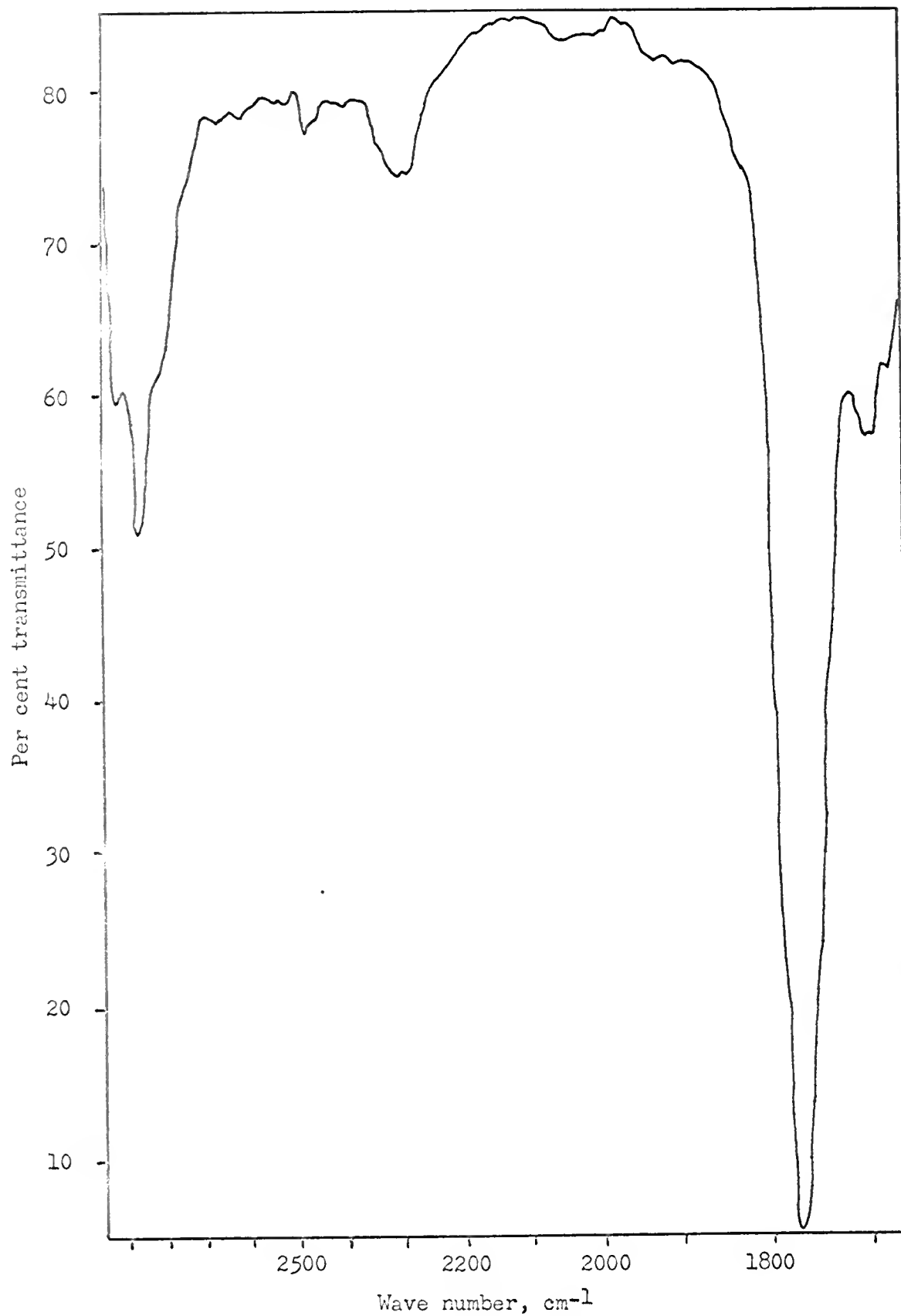


Fig. 12.--Infrared spectrum of $(\text{CH}_3)_3\text{NBD}_3$.

Preparation of B_2D_6 from $(CH_3)_3NBD_3$ and $BF_3(g)$

Trimethylamine borane- d_3 (4.0 mmoles) was sublimed into a reaction tube fitted with a stopcock and a side arm filled with mercury such that if the tube were inverted the mercury sealed the stopcock from the contents of the tube. Boron trifluoride gas was entered into the vacuum system from the storage tank. The gas was purified by distilling from a CCl_4 - $CHCl_3$ - $CO_2(s)$ trap (-78°), through an ethylbromide slush (-119°), into a liquid N_2 bath (-196°), before condensing into the reaction tube. The reaction tube was then warmed to room temperature and set aside for an extended period of time.

A liquid phase was present in the reaction tube after the tube warmed to room temperature, but the liquid phase slowly disappeared.^a After eighty to ninety hours at room temperature, the reaction tube was attached to the vacuum system, the products condensed in liquid N_2 , and any non-condensable gas removed. The reaction tube was then warmed to -78° and the volatile fraction was removed and condensed onto excess anhydrous diethylether. Any unreacted $BF_3(g)$ would form the etherate and the B_2D_6 could be separated from it. The ether flask was warmed to -78° and a product, B_2D_6 ,

^aUsually this occurred overnight. Care must be taken to prevent this liquid phase from holding the mercury next to the stopcock on solidifying and thus sealing all gaseous product in the tube.

was distilled from a -78° bath, through a -119° bath, into a -196° bath. The distillation was done rapidly to prevent contamination of the B_2D_6 with ether vapor. The material in the -196° trap was diborane- d_6 .

The results of the experiments were as follows in Table 6.

TABLE 6
REACTION OF $(CH_3)_3NBD_3$ AND $BF_3(g)$

| Compound | Mmoles | Yield mmoles | Yield Per Cent | Vapor Pres- sure at CS_2 Slush ^a |
|-----------------|--------|-----------------|-------------------|---|
| $(CH_3)_3NBD_3$ | 4.00 | 1.64 | 82.0 | 239.0 mm |
| $BF_3(g)$ | 5.71 | | | |
| $(CH_3)_3NBD_3$ | 2.11 | 0.90 | 84.9 | 238.5 mm |
| $BF_3(g)$ | 3.78 | | | |

^aLiterature value is 238.3 mm (6).

The infrared spectrum of the B_2D_6 was in agreement with the reported spectrum (43). The resolution of the spectrum (Figure 13) was poor but it did show a low intensity at 2500 cm^{-1} which was due to a BH stretching vibration, and the intense BD stretching vibrations at $1810\text{--}1840\text{ cm}^{-1}$ and 1954 cm^{-1} . A rough estimate of the concentration of BH to BD from Beer's law gave a ratio for C_{BH}/C_{BD} of 0.15. The absorptivity of BH and BD were assumed to be equal in this calculation.

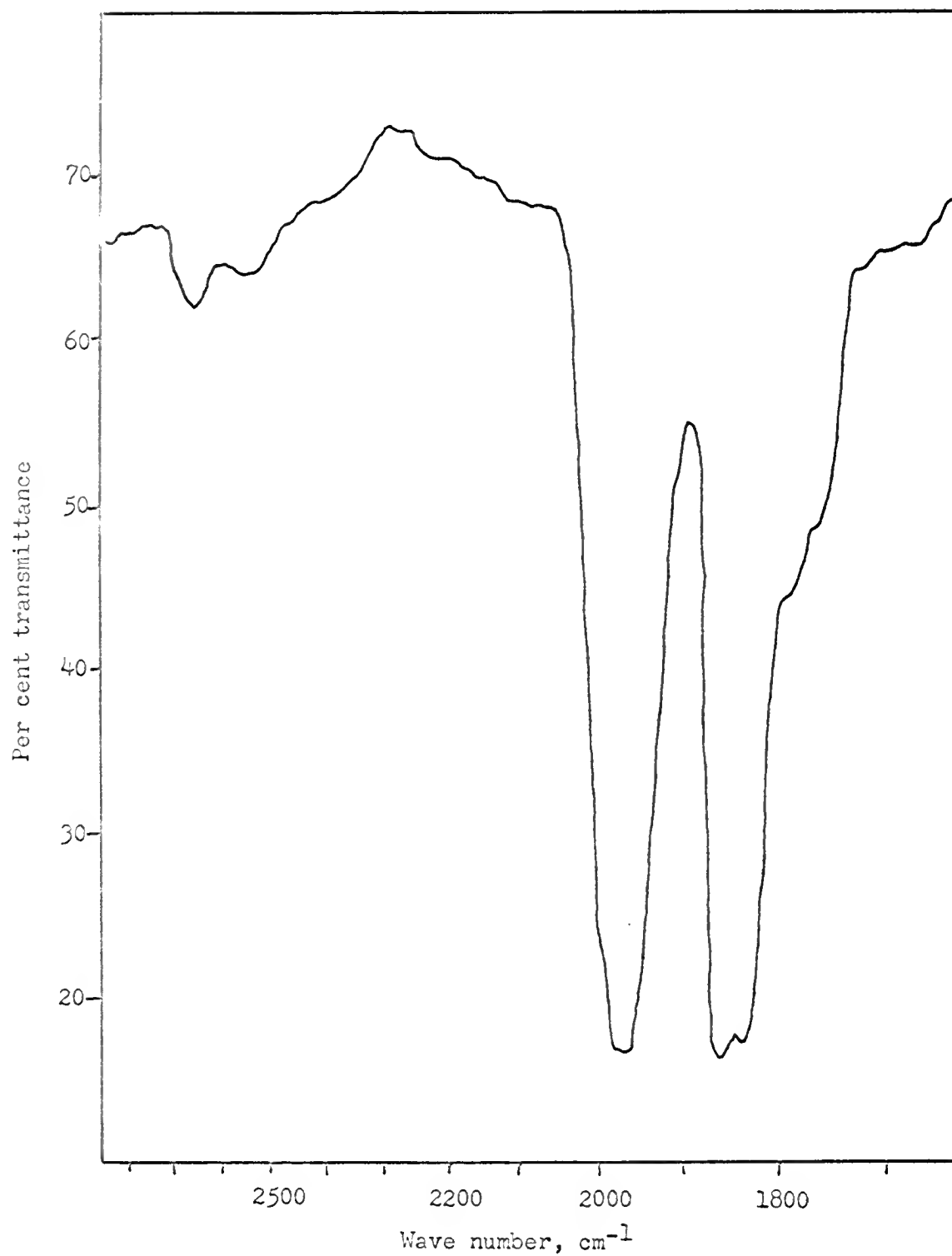
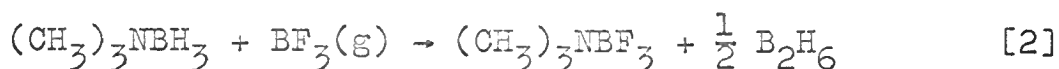


Fig. 13.--Infrared spectrum of B_2D_6 .

A sample of the diborane-d₆ was pyrolyzed and a mass spectrum run on the products. For the results of this experiment see Table 2.

Variation in the per cent reaction of (CH₃)₃NBH₃ and BF₃(g) to yield B₂H₆

Boron trifluoride will displace diborane from trimethylamine borane according to the equation (28):



The extent of this reaction in mercury-sealed bulbs was studied as a function of time in order to determine the optimum time for the practical synthesis of diborane at room temperature. The following variations, listed in Table 7, in the per cent reaction were determined.

The extent of reaction was followed by measuring the total pressure in the reaction flask as a function of time. For complete reaction, the total pressure should be one half of the initial pressure according to equation [2]. The graphs (Figures 14 and 15) showing the variation in total pressure with time indicated that after fifty hours the reaction, for practical purposes, was complete since the additional amount of diborane produced in the next thirty hours did not warrant the extra time spent. The plots indicated little difference in the rate of decrease in total pressure

TABLE 7
REACTION OF $(\text{CH}_3)_3\text{NBH}_3$ AND $\text{BF}_3(\text{g})$

| Compound $(\text{CH}_3)_3\text{NBH}_3$ mmoles | + $\text{BF}_3(\text{g})$ mmoles | B_2H_6 mmoles | Per Cent Yield | Time Hours | Vapor Pressure B_2H_6^a |
|---|-------------------------------------|----------------------------------|-------------------|---------------|---|
| 3.19 | 2.52 | 0.79 | 62.5 | 19.5 | 224 |
| 2.25 | 2.55 | 0.47 | 42.2 | 13.3 | 222 |
| 2.07 | 2.54 | 0.67 | 64.6 | 60.5 | 224 |
| 3.06 | 2.50 | 0.88 | 70.6 | 79.3 | 224 |
| 2.06 | 2.47 | 0.83 | 80.7 | >79.3 | 224 |
| $(\text{CH}_3)_3\text{NBD}_3$ | $\text{BF}_3(\text{g})$ | B_2D_6 | | | B_2D_6 |
| 2.72 | 3.63 | 1.03 | 75.6 | ~96 | 236 |
| 4.00 | 5.71 | 1.64 | 82.0 | 92 | 239 |
| 2.11 | 3.78 | 0.90 | 85.1 | 85 | 238.5 |

^aAt carbon disulfide slush temperature. The literature values (6) were 225 mm for B_2H_6 and 238.3 mm for B_2D_6 .

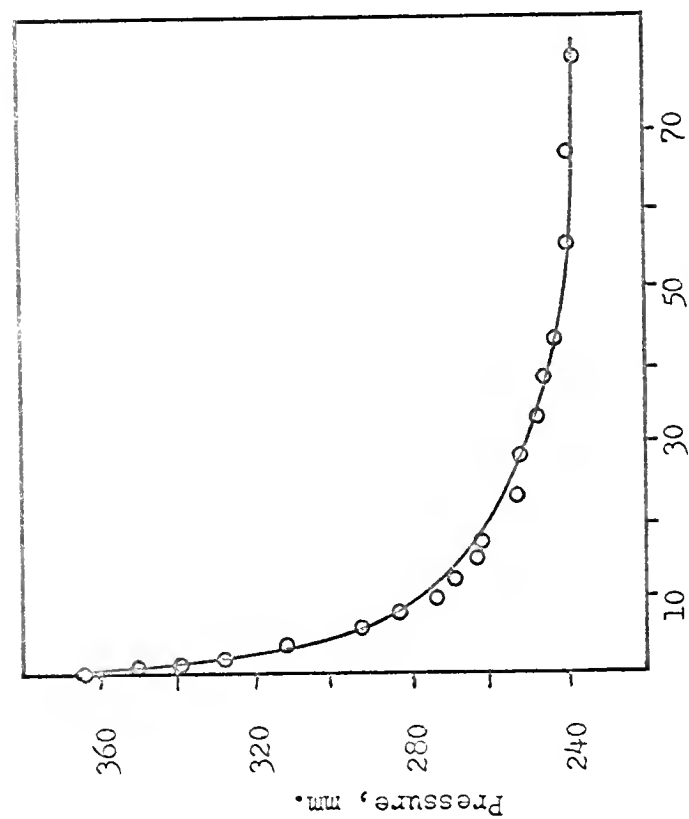


Fig. 14.--Change in total pressure with time for the reaction of excess $(\text{CH}_3)_3\text{NBH}_3$ and $\text{BF}_3(\text{g})$.

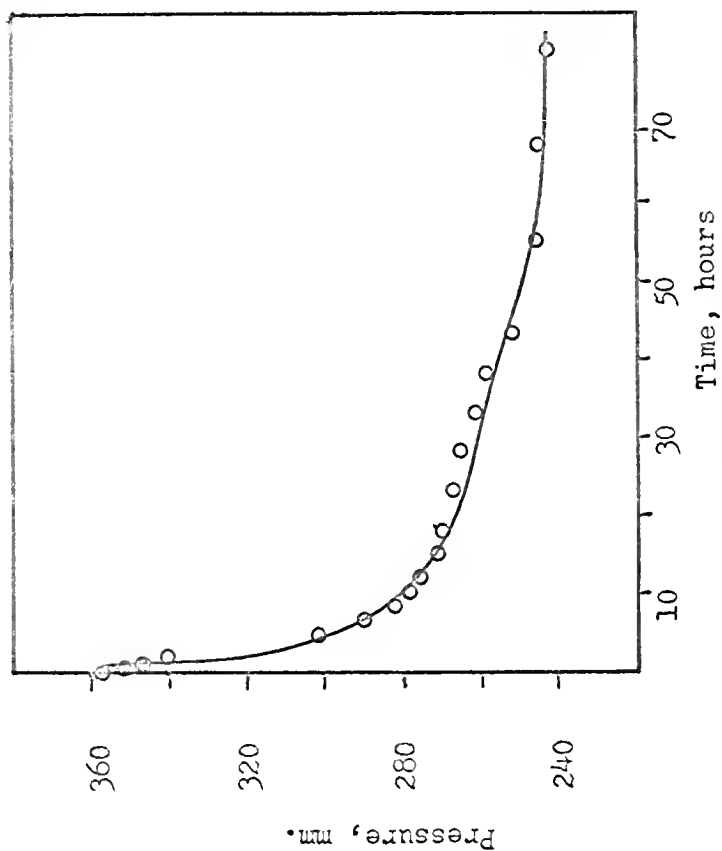
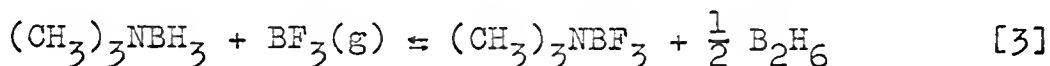


Fig. 15.--Change in total pressure with time for the reaction of $(\text{CH}_3)_3\text{NBH}_3$ and excess $\text{BF}_3(\text{g})$.

with time whether $\text{BF}_3(\text{g})$ or $(\text{CH}_3)_3\text{NBH}_3$ were in excess, although the sample containing excess $\text{BF}_3(\text{g})$ had a 10 per cent greater extent of reaction.

The data implied that at room temperature the reaction was only 85 per cent complete in eighty to ninety hours. It could be possible for the reaction mixture to reach an equilibrium state in which B_2H_6 was displacing $\text{BF}_3(\text{g})$ in the reverse reaction according to the equation:



An equilibrium such as this could explain the small change in total pressure after sixty hours. The attainment of an equilibrium state is supported by the work of Miller and Onyszchuk (28), who found in forty-five minutes at $130^\circ\text{--}140^\circ$ an average displacement of 23.4 per cent $\text{BF}_3(\text{g})$ in $(\text{CH}_3)_3\text{NBF}_3$ by B_2H_6 and an average displacement of 83.3 per cent B_2H_6 from $(\text{CH}_3)_3\text{NBH}_3$ by $\text{BF}_3(\text{g})$. However, Graham and Stone (17) reported that after heating B_2H_6 and $(\text{CH}_3)_3\text{NBF}_3$ for twelve hours at 80° the gas did not show any evidence of BF_3 in the infrared spectrum. They concluded that no reaction had occurred under these conditions. The implications appear to be that for the equilibrium to be established, the temperature must be greater than 80° or the time must be longer than twelve hours. But the data show that the rate of displacement depends greatly on temperature. Miller and

Onyszchuk (27) achieved the same per cent displacement in forty-five minutes at 130°-140° that we obtained in approximately ninety hours at room temperature (23°-25°).

The displacement reaction proved to be an impractical method for preparing diborane. It was used in this work to prepare deuterated diborane. R. E. Davis (11) had reported the exchange of boron hydrogens in trimethylamine borane with acidic D₂O to be rapid and quantitative. In this manner, (CH₃)₃NBD₃ could be prepared and then B₂D₆ displaced from the adduct by BF₃(g). Thus, B₂D₆ could be prepared from readily available and inexpensive starting materials, without the use of deuterium gas to deuterate the diborane, or without the use of a borodeuteride salt.

The displacement reaction did not give diborane of sufficiently high deuterium content and B₂D₆ was prepared afterwards with NaBD₄ as the source of deuterium.

Preparation of B₂D₆ from NaBD₄ and BF₃(g) in diglyme (4)

Sodium borodeuteride (1.0 gram) was placed in a 100 ml round bottom reaction flask in the Dri-Lab controlled atmosphere box.^a A stopcock adapter for attaching the flask to the vacuum system was added to the reaction flask. The flask was then attached to the vacuum system and was evacuated.

^aA static charge on the powdered NaBD₄ prevented a quantitative transfer of the material from the glassine weighing paper into the flask.

The diglyme (ethylene glycol dimethyl ether) to be used as the solvent was refluxed and distilled from sodium metal, again distilled from LiAlH_4 , and finally transferred from LiAlH_4 under vacuum into the reaction flask at -196°C .

Boron trifluoride was condensed into the vacuum system directly from the storage tank. The BF_3 was then purified by distilling it from a $\text{CCl}_4\text{-CHCl}_3\text{-CO}_2$ trap (-78°) through an ethyl bromide slush trap (-119°) into a liquid N_2 trap (-196°). The gas was then condensed into the reaction flask submerged in a liquid N_2 bath. A total of 53.14 mmoles of BF_3 was condensed into the reaction flask. The molar ratio of $\text{BF}_3(\text{g}) : \text{NaBD}_4$ was 2.2:1.

The reaction flask was allowed to warm to room temperature (22°). After thirty minutes, the reaction was cooled to -78° and the volatile fraction removed into a -196° trap. This procedure was repeated twice with reaction times at 22° of thirty minutes and sixty minutes. The total amount of volatile material removed from the reaction flask was 10.76 mmoles. The material had a vapor pressure of 254.0 mm at carbon disulfide slush temperature (-111.9°). The literature value (6) for the vapor pressure of B_2D_6 at this temperature was 238.5 mm.

To remove any possible BF_3 impurity in the B_2D_6 , the gas was condensed onto anhydrous diethyl ether. The gas-diethyl ether mixture was warmed to -78° and the volatile

portion was transferred into a liquid N_2 trap. After thirty minutes, 10.55 mmoles of volatile material had transferred from the ether flask. This material had a vapor pressure of 238.5 mm in a carbon disulfide slush bath, in agreement with the previously cited literature value.

An infrared spectrum was run on the material before it was reacted with ether. The spectrum was in agreement with that reported for B_2D_6 (43). No spectral evidence was noted for the impurity which was removed by the diethyl ether. There was a low intensity peak at 2510 cm^{-1} . A rough estimate using Beer's law showed, that according to this BH peak, the ratio of $C_{BH} : C_{BD}$ was 0.058 assuming that the absorptivity for BH and BD are equal. The assumption was correct for the absorptions in the infrared spectra of $(CH_3)_3NBH_3$ and $(CH_3)_3NBD_3$.

A sample of this B_2D_6 was pyrolyzed and a mass spectrum run on the non-condensable products. For the results of this experiment see Table 2.

Preparation of B_2H_6 from $NaBH_4$ and $BF_3(g)$ in diglyme

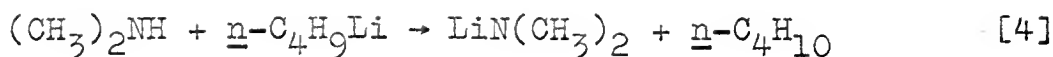
This preparation was done in the same manner as the preparation of B_2D_6 from $NaBD_4$ and $BF_3(g)$ in diglyme. The amounts of reagents used were 0.4 g (10.58 mmoles) $NaBH_4$ and 22.25 mmoles $BF_3(g)$. The molar ratio of $BF_3(g) : NaBH_4$ was 2.1:1.

A product was isolated in 78.7 per cent yield (7.05 mmoles) which had a vapor pressure of 225 mm at carbon disulfide slush temperature. The reported value (6) at this temperature is 225 mm. An infrared spectrum of this compound was identical with that reported for B_2H_6 in the literature (43).

General procedure for preparation of $(CH_3)_2ND$

A solution of n-butyl lithium in n-hexane (1.6 M) was syringed into a 100 ml round bottom flask under a stream of nitrogen. An adapter to the vacuum system was inserted immediately into the flask, the contents were condensed in a liquid N_2 bath, and the flask evacuated. Excess dimethylamine which had been stored over sodium metal was condensed into the flask containing the hexane solution.

The reaction flask was then warmed to room temperature and immediately a white precipitate appeared. After thirty minutes at room temperature, the reaction flask was cooled to 0° for thirty minutes, and then a volatile fraction was removed into a liquid N_2 trap. The transfer was done slowly to prevent excessive spattering of the white solid as the liquid phase was removed. The remaining excess dimethylamine, n-butane, and n-hexane were removed with the flask at room temperature. A white solid residue, $LiN(CH_3)_2$, remained in the flask, according to the equation:



A vial equipped with a capillary break-off tip containing deuterium oxide (1 ml) was attached to the vacuum system, the tip of the vial was broken and the D_2O condensed onto the amide salt in a liquid N_2 bath. The reaction flask was slowly warmed to room temperature and an immediate increase in pressure was noted. The white solid had turned dark brown after fifteen minutes at room temperature. Part of the flask was cooled to 0° and kept at this temperature for one hour and forty-five minutes. All the volatile material in the reaction flask was transferred into a flask containing excess anhydrous potassium carbonate in a liquid N_2 bath. The K_2CO_3 flask was warmed to 0° in an ice bath and kept at this temperature for two hours. The K_2CO_3 mixture was then cooled to -78° and a volatile fraction removed into a liquid N_2 trap, requiring approximately forty-five minutes. This material was deuterated dimethylamine. A possible impurity in this material would be monodeuterated n-butane due to incomplete reaction of the n-butyl lithium and the dimethylamine according to equation [4].

The results of the experiments are as shown in Table 8.

TABLE 8
PREPARATIONS OF $(\text{CH}_3)_3\text{ND}$

| 1.6M n-Butyl Lithium | $(\text{CH}_3)_2\text{NH}$ mmoles excess | Recovered $(\text{CH}_3)_3\text{ND}$ | Per Cent Yield | Vapor Pressure ^a at 0° |
|-------------------------|--|---|----------------------|---|
| 10 ml | 22.7 | 13.7 | 85.8 | 575.5 |
| 10 ml | 25.6 | 15.1 | 94.4 | 549.5 |
| 10 ml | excess ^b | 12.7 | 79.1 | >760 |

^aLiterature value (38) was 547.5 mm.

^bReaction flask at liq N_2 temperature was open to portion of vacuum system in which the amount of $(\text{CH}_3)_2\text{NH}$ was being measured. Therefore, it was not possible to determine the exact amount of $(\text{CH}_3)_2\text{NH}$ entered into the reaction flask.

Gas phase infrared spectra of these different preparations were identical. The spectra were similar to the spectrum of undeuterated dimethylamine (34) except for some shifting of peaks in the 1300 cm^{-1} to 1000 cm^{-1} region. The deuterated amine which had a vapor pressure at 0° greater than 760mm did have an extra peak at 2150 cm^{-1} . An attempt to purify this sample by distilling a fraction from an ethylbromide slush (-119°) into a liquid N_2 trap resulted in an increase in intensity in the infrared spectrum of the peak at 2150 cm^{-1} in the fraction which transferred into the liquid N_2 trap. The infrared absorption peaks of n-butane (20) were not detectable in the spectrum. The peak at 2150 cm^{-1} could be attributed to a C-D stretching frequency in monodeuterated n-butane. The C-D stretching frequency in the deuterated methanes varies from 2085 cm^{-1} in CD_4 to 2205 cm^{-1} in DCH_3 (29). This material was more volatile than the amine, which was consistent with the relative vapor pressures of dimethylamine and n-butane. n-Butane has a higher vapor pressure than dimethylamine (8).

General method for the preparation of $(\text{CH}_3)_2\text{HNBH}_3$ from B_2H_6 and $(\text{CH}_3)_2\text{NH}$

Diborane and an excess of dimethylamine were condensed into a 50 ml round bottom flask in a liquid nitrogen bath. A $\text{CCl}_4\text{-CHCl}_3\text{-CO}_2(\text{s})$ bath (-78°) was then placed about the

flask and it remained at this temperature for an extended period of time (for the exact reaction times see Table 9). The excess amine was removed from the flask at 0° into a liquid N₂ trap, and the liquid product remaining in the flask slowly solidified on storage at room temperature.

Mass spectra of the boranes showed a mass peak of low intensity corresponding to the mass to charge ratio of the parent ion, and a high intensity peak at a mass to charge ratio corresponding to the loss of a hydrogen or deuterium atom.

The results of the preparations of the variously deuterated dimethylamineboranes are given in Table 9. For the method of analysis see page 5. The infrared spectra are given in Figures 2, 4 and 5.

Each of the variably deuterated dimethylamine boranes was heated at 100-102° and the non-condensable reaction product analyzed in the mass spectrometer for the percentages of D₂, HD, and H₂. The results of these elimination reactions are given in Table 10.

The infrared spectrum of the compounds in carbon tetrachloride solution, in each case, contained peaks where the NH, ND, BH, and BD stretching vibrations occur. Beer's law was used to calculate the relative percentages of each compound using the CH deformation absorption as the internal reference. For the results see Table 3.

TABLE 9

PREPARATION OF $(\text{CH}_3)_2\text{HNBH}_3$ CONTAINING VARIOUS DISTRIBUTIONS OF
HYDROGEN ISOTOPES

| Diborane (mmoles) | Amine (mmoles) | Reaction time Reaction tempera- ture | Amine recovered over that re- quired for 1:1 adducts ^a | Ratio |
|--------------------------------|-------------------------------------|--|--|------------------------------|
| B_2D_6 4.56 | $(\text{CH}_3)_2\text{ND}$ 16.2 | ^c 4 days/ -78° | +0.68 mmoles calculated found | 1:1:3 1:1:2.95 |
| B_2D_6 2.43 | $(\text{CH}_3)_2\text{ND}$ 12.68 | 45 min. 20 min. -78° 0° | -0.52 calculated found | 1:1:3 1:1:2.96 |
| B_2D_6 5.87 | $(\text{CH}_3)_2\text{NH}$ 25.46 | ^c 4 days/ -78° | +0.11 calculated found | 1:1:3 1:1:2.97 |
| B_2H_6 5.55 | $(\text{CH}_3)_2\text{ND}$ 12.66 | 24 hours -78° | -0.46 calculated found ^b | 1:1:3 1:1:-- ^d |

^aEquation $\frac{1}{2}\text{B}_2\text{H}_6 + (\text{CH}_3)_2\text{NH} \rightarrow (\text{CH}_3)_2\text{HNBH}_3$.

^bWeight of this sample was questionable.

^cDue to break in vacuum system.

^dHydrolysis flask leaked during the reaction.

TABLE 10
RESULTS OF HEATING $(\text{CH}_3)_2\text{HNBH}_3$ CONTAINING VARIOUS
DISTRIBUTIONS OF HYDROGEN ISOTOPES

| | Compound | Mmoles | Time | Per Cent Reaction | Per Cent | |
|---|---------------------------------|--------|----------|----------------------|----------------|----------------|
| | | | | | D ₂ | H ₂ |
| 1 | $(\text{CH}_3)_2\text{DNBD}_3$ | 1.05 | 24 hours | 38.1 | 83.1 | 16.9 |
| 2 | $(\text{CH}_3)_2\text{DNBD}_3$ | 1.47 | 2 hours | 3.9 | 60.5 | 39.5 |
| 3 | $(\text{CH}_3)_2\text{HNBBD}_3$ | 1.16 | 2 hours | 5.4 | 8.9 | 78.4 |
| 4 | $(\text{CH}_3)_2\text{DNBH}_3$ | 1.76 | 2 hours | 4.9 | 4.0 | 54.3 |
| | | | | | | 41.7 |

Preparation of $(\text{CH}_3)_2\text{DNBH}_3$ from $(\text{CH}_3)_2\text{ND}_2\text{Cl}$ and LiBH_4

N-Deuterodimethylammonium chloride was prepared by condensing N-deuterodimethyl amine (7.67 mmoles) into a tared 50 ml round bottom flask containing deuterium oxide (1 ml) and thionyl chloride (15 mmoles).^a The reaction flask was warmed to 0°. After one and one-half hours, all volatile material was removed from the flask. The increase in weight of the reaction flask implied that only 0.86 mmoles of product was formed. The volatile material was transferred back to the reaction flask.

A gas phase infrared spectrum of the most volatile materials in the reaction flask was identical to that of $\text{SO}_2(\text{g})$ (3) and mono-deuterated n-butane which was known to be a contaminant in the $(\text{CH}_3)_2\text{ND}$ used. The n-butane and some of the $\text{SO}_2(\text{g})$ was transferred from the flask at -78° into a -196° trap in thirty minutes.

More deuterium oxide (1 ml, making a total of 2 ml) was distilled into the reaction flask and dimethylamine (6.3 mmoles) was condensed into the flask. After forty-five minutes at 0° and thirty minutes at 25°, all the volatile material was removed; the weight gain by the reaction flask implied 6.48 mmoles dimethylammonium chloride had formed.

^aThe hydrogen chloride impurity in the thionyl chloride was removed by warming the thionyl chloride to -78° and exposing it to a -196° trap for twenty-five minutes.

The ion should have been almost completely deuterated since $(\text{CH}_3)_2\text{NH}_2^+$ is known (38) to exchange rapidly with the solvent in acidic solution and a large excess of heavy water had been used. The infrared spectrum in a Nujol mull contained absorptions in the 1900-2400 cm^{-1} region and none greater than 3000 cm^{-1} , indicating the absence of NH absorption. The completely deuterated ammonium ion has absorptions at 2214 and 2346 cm^{-1} (30). Therefore, the product should be primarily the deuterium-containing material.

In the Dri-Lab controlled atmosphere box, lithium borohydride (approximately 11.5 mmoles) was added to the flask containing the $(\text{CH}_3)_2\text{ND}_2\text{Cl}$. The flask was attached to a vacuum system and approximately 25 ml of diethylether (stored over CaH_2) was distilled into the flask. After forty-five minutes at 0° and fifteen minutes at room temperature, no evidence for reaction was noted. The reaction flask was returned to the Dri-Lab and LiBH_4 from another bottle added to the solution. Immediate gas evolution was noticed. Excess LiBH_4 was added and the solution was magnetically stirred. After one hour when no more gas evolution was noticed, the reaction mixture was filtered and the residue washed with approximately 10 ml of ether. After the ether was removed by vacuum distillation, a liquid phase containing a white solid remained in the flask.

A small amount of the liquid product was vacuum distilled from the reaction flask at room temperature into a -196° trap. An infrared spectrum of this material showed absorptions at 3210 cm^{-1} (NH), $2300\text{--}2400\text{ cm}^{-1}$ (ND, BH), and at 1750 cm^{-1} (BD). Since the material distilled so slowly, it was recrystallized from cold carbon tetrachloride and *n*-hexane. The recrystallized product was a solid at room temperature. It was placed in a vacuum sublimation apparatus, and the most volatile fraction was removed by pumping on the sublimator at room temperature and collecting a product in a -196° trap. After twenty-five minutes, the cold finger in the sublimator was cooled to -78° with $\text{CO}_2(\text{s})$ and the material was collected for nine hours. The initial material removed from the sublimator into the -196° trap was a liquid at room temperature and the compound collected on the cold finger was a solid at room temperature. The infrared spectra (Figure 16) of the recrystallized compound and on the fractions obtained by sublimation were identical and showed absorptions in the same regions as the material initially transferred from the reaction flask. The percentages of NH and BD bond in the compound were calculated from the infrared spectra using Beer's law. The percentages were calculated relative to the CH deformation at 1475 cm^{-1} as the internal reference. The results were given in Table 11.

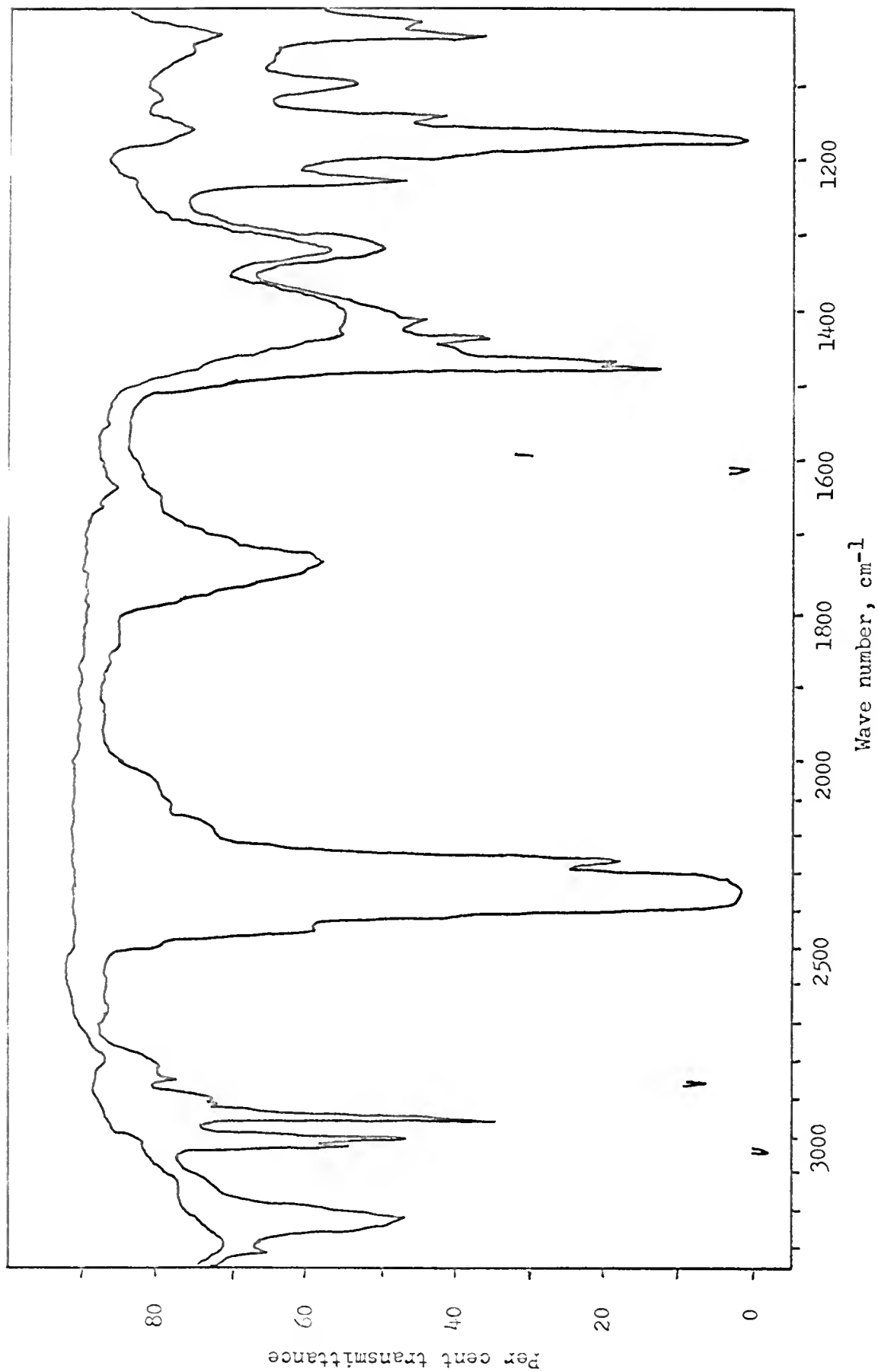


Fig. 16.--Infrared spectrum of $(\text{CH}_3)_2\text{DNBH}_3$ prepared from $(\text{CH}_3)_2\text{ND}_2\text{Cl}$ and LiBH_4 .

TABLE 11

PER CENT BD AND NH BONDS IN $(\text{CH}_3)_2\text{DNBH}_3$ PREPARED
FROM $(\text{CH}_3)_2\text{ND}_2\text{Cl}$ AND LiBH_4

| Compound: | $(\text{CH}_3)_2\text{DNBH}_3$ | | Per Cent | Per Cent |
|---|--------------------------------|--------|----------|----------|
| | BD | NH | BD | NH |
| Fraction | Absorbency | | | |
| Sublimed from Reaction Flask | 0.342 | 0.201 | 18.0 | 20.2 |
| Recrystallized CCl_4 - <u>n</u> -hexane | 0.0492 | 0.0492 | 14.7 | 28.0 |
| Recrystallized First Fraction from Sublima- tion | 0.0453 | 0.0414 | 13.3 | 23.3 |
| Recrystallized and Collected on Cold Finger | 0.155 | 0.167 | 13.2 | 27.2 |

Any dimethylaminoborane impurity should be contained in the initial fraction sublimed from the reaction flask.^a A small impurity of this compound in the spectrum would cause a low percentage of NH relative to CH in the calculation, and the absorption at 1750 cm^{-1} in the spectrum of dimethylaminoborane would cause a high percentage of BD relative to CH to be calculated. Another source of error would be in using the absorptivity ratio of BH:CH in $(\text{CH}_3)_2\text{HNBH}_3$ to calculate the per cent BD, the assumption made here has been shown previously^b to be a questionable one. The first fraction sublimed from the recrystallized compound could also contain an aminoborane impurity. The percentage of BD and NH containing compounds show that some fractionation was accomplished by the method of purification, but still the recrystallized material before and after sublimation were essentially the same.

The larger percentage of NH bonds compared to BD bonds would indicate that hydrogen-deuterium exchange occurred before the formation of the aminoborane. Thus, this method of preparation, under the experimental conditions used, did not give a pure product containing deuterium

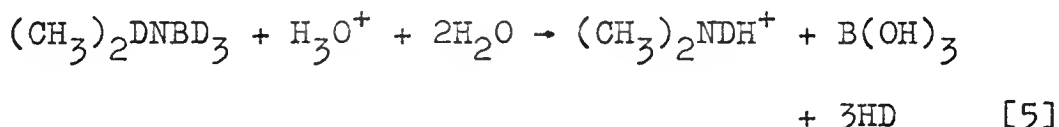
^aDimethylaminoborane has a vapor pressure of 10mm at 23° (39).

^bSee page 17.

only on the nitrogen atom, due to the exchange between ND and BD bonds prior to the reaction to form the amine borane.

Hydrolysis of $(\text{CH}_3)_2\text{DNBD}_3$ in 0.1 M hydrochloric acid

N-Deuterodimethylamine borane- d_3 (0.914 mmoles) was sublimed into a 50 ml round bottom reaction flask and hydrochloric acid (20 ml of 0.1 M) was distilled into the flask. After nine hours at room temperature, the reaction product was condensed and the non-condensable gas removed with a Toepler pump. The amount of non-condensable gas (2.70 mmoles) corresponded to complete reaction according to the equation:



The mass spectrum of the non-condensable gas gave 14 per cent HD and 86 per cent H_2 . The 14 per cent HD in the non-condensable hydrolysis product indicated that the rate of exchange of BD with the solvent was not so much more rapid than the rate of solvolysis that all of the deuterium bonded to boron exchanged before the solvolysis reaction was complete.

R. E. Davis (11) reported only H_2 gas produced in the acid hydrolysis of $(\text{CH}_3)_3\text{NBD}_3$ due to the rapid acid catalyzed exchange of the BD with the solvent. However, the rate of

acid hydrolysis of $(\text{CH}_3)_2\text{HNBH}_3$ is greater than that of $(\text{CH}_3)_3\text{NBH}_3$ (24). Therefore, the BD in $(\text{CH}_3)_3\text{NBD}_3$ would have had more time to exchange before solvolysis than in $(\text{CH}_3)_2\text{HNBD}_3$.

H. C. Kelly (23) reported that for *p*-toluidine borane- d_3 in a 50/50 mixture of dioxane and water with no acid present, the rate of exchange of BD with solvent was negligible relative to the rate of solvolysis; but that at high acid concentrations the rate of exchange increased. Kelly found no primary hydrogen isotope effects in the solvolysis reaction.

Determination of reaction conditions for the hydrogen elimination reactions

Dimethylamine borane was heated in sealed glass tubes for various periods of time and the amount of hydrogen eliminated measured by transferring the hydrogen into a calibrated bulb with a Toepler pump. The temperature of 100° was used for the reactions because it gave a reasonable rate of hydrogen evolution. In general, the extent of reaction at low percentages was not very reproducible, since the small amounts of hydrogen being measured (usually 0.4 mmoles or 0.03 mmoles in a volume of 105.8 ml) were subject to experimental error.

The results of the experiments were given in Table 12. These experiments led to the selection of reaction

TABLE 12
REACTION CONDITIONS FOR H₂ ELIMINATION REACTIONS

| $(\text{CH}_3)_2\text{HNBH}_3$ mmoles | Time (hour) | Temperatures | Per Cent Reaction |
|--|----------------|--------------|----------------------|
| 1.54 | 1 | 100° | 13.5 |
| 1.47 | 1 | 70° | 2.32 |
| 0.99 | 10 | 100° | 42.8 |
| 2.40 | 3 | 100° | 15.8 |
| 2.20 | 1 | 105° | 16.4 |
| 2.45 | 0.33 | 100° | 1.02 |
| 2.80 | 0.66 | 100° | 1.54 |
| 2.57 | 0.83 | 101° | 12.8 |
| 2.22 | 0.66 | 100° | 2.1 |
| 2.18 | 0.75 | 100° | 2.5 |
| 2.07 + trace $(\text{CH}_3)\text{NH}$ | 0.75 | 100° | 2.2 |
| 2.45 | 0.83 | 100° | 2.2 |

times of twenty-four hours in the initial experiment of heating $(\text{CH}_3)_2\text{DNBD}_3$ with $(\text{CH}_3)_2\text{HNBH}_3$ and of a time of one hour in the experiments where just the initial reaction products were desired in an attempt to ascertain a kinetic isotope effect.

A trace of free dimethylamine added to one of the reaction tubes did not significantly affect the extent of reaction.

Hydrogen elimination on heating dimethylamine boranes

Dimethylamine borane was sublimed from a storage flask into a reaction tube equipped with a capillary break-off tip. The amount of compound sublimed into the reaction tube was determined by weighing the storage bulb before and after the sublimation. Then a second dimethylamine borane, containing a different isotopic distribution of hydrogen atoms on boron and nitrogen, was sublimed into the reaction tube, and the tube sealed off with a torch. In a typical experiment, approximately one mmole of each compound was used. The reaction tubes were heated at $100 \pm 2^\circ\text{C}$ for the desired reaction time. After rapid cooling the non-condensable gas was transferred into a bulb by using the Toepler pump. The gas samples were stored at room temperature until analysis in the mass spectrometer.

The results of these experiments were given in Table 13.

TABLE 13

RESULTS OF HYDROGEN ELIMINATION BY DINETHYLAMINE BORANES

| Compounds mmoles | Time | Per Cent Reaction | Per Cent | |
|--|---------|----------------------|----------------|----------------|
| | | | D ₂ | H ₂ |
| (CH ₃) ₂ DNBD ₃ + (CH ₃) ₂ HNBH ₃ | | | | |
| 0.82 | 24 hrs. | 31.3 | 11.0 | 41.3 |
| 0.58 | 24 hrs. | 43.2 | 10.2 | 45.0 |
| (CH ₃) ₂ DNBH ₃ + (CH ₃) ₂ HNBBD ₃ | | | | |
| 0.50 | 24 hrs. | 32.8 | 12.9 | 40.6 |
| 1.05 | 24 hrs. | --- | 16.4 | 36.1 |
| (CH ₃) ₂ HNBBD ₃ + (CH ₃) ₂ DNBD ₃ | | | | |
| 1.02 | 1 hr. | 1.3 | 25.4 | 9.6 |
| 0.91 | 1 hr. | 1.9 | 20.8 | 26.2 |
| (CH ₃) ₂ DNBH ₃ + (CH ₃) ₂ HNBH ₃ | | | | |
| 1.07 | 1 hr. | 2.8 | -- | 82.6 |
| 1.02 | 1 hr. | 4.7 | -- | 83.7 |

Table 13 (cont'd)

| Table 12 (cont'd.) | | | | |
|--|-------|----------------------|----------------|----------------|
| Compounds mmoles | Time | Per Cent Reaction | Per Cent | |
| | | | D ₂ | H ₂ |
| (CH ₃) ₂ DNBH ₃ + (CH ₃) ₂ DNBD ₃ | | | | |
| 1.03 | 1 hr. | 1.4 | 32.9 | 21.4 |
| 1.06 | 1 hr. | 9.7 | 23.6 | 30.6 |
| (CH ₃) ₂ HNBBD ₃ + (CH ₃) ₂ HNBH ₃ | | | | |
| 0.96 | 1 hr. | 1.7 | 2.2 | 42.1 |
| 0.96 | 1 hr. | 2.8 | 2.4 | 44.0 |
| | | | | 55.7 |
| | | | | 53.6 |

Experiments to eliminate possibility of isotopic interchange during the elimination reactions

I. Heating of D_2 and H_2 in the presence of mercury

vapor.--A bulb was attached to the vacuum system, evacuated, and submerged in a liquid N_2 bath. After condensing mercury vapor into the bulb for ten hours, approximately equal moles of hydrogen and deuterium were placed in the bulb. The bulb was closed and heated at 100° for twenty-four hours. The gas was analyzed by the mass spectrometer and shown to be only hydrogen and deuterium. No exchange of the H_2 and D_2 occurred under these conditions. Therefore, it was concluded that the reaction gases did not exchange among themselves, even in the presence of mercury vapor.

II. Heating D_2 with $(CH_3)_2HNBH_3$ and $(CH_3)_3NBH_3$ to

determine if exchange occurred.--The amine borane was placed in a tube with a capillary break-off tip, condensed in liquid N_2 and evacuated. Deuterium (150 mm) was placed in the tube and the tube glass sealed. The tube was heated at 100° for one hour and then a sample of the gas removed from the tube by breaking the tip and allowing the gas to expand into a bulb. The gas was analyzed in the mass spectrometer to determine if any HD had been produced. The gaseous product did not contain any material with a m/e of 3 according to the mass spectral analysis. The solid materials

were dissolved in spectral grade carbon tetrachloride and the infrared spectra (Figures 17 and 18) determined. The spectra showed no absorption whatever at $1750\text{--}1800\text{ cm}^{-1}$, where BD absorbs intensely, but were identical to the spectra of $(\text{CH}_3)_2\text{HNBH}_3$ and $(\text{CH}_3)_3\text{NBH}_3$.

The experiments were repeated heating the deuterium-amineborane mixtures for twenty-four hours. The infrared spectra in both cases contained absorptions in the $1700\text{--}1800\text{ cm}^{-1}$ range. The spectrum (Figure 19) of $(\text{CH}_3)_2\text{HNBH}_3$ and D_2 after heating had weak absorptions at 1725 and 1850 cm^{-1} , and an intense absorption at 1785 cm^{-1} which is where the BD stretching vibration occurs. The spectrum (Figure 20) of $(\text{CH}_3)_3\text{NBH}_3$ and D_2 after heating had a medium absorption at $1740\text{--}1750\text{ cm}^{-1}$.

An infrared spectrum (Figure 6) was taken of $(\text{CH}_3)_2\text{HNBH}_3$ after thirty-four hours at 100° and the spectrum had a medium absorption at 1750 cm^{-1} . This absorption must be due to some reaction product and not to a BD vibration since there was no deuterium in the molecule or in contact with it. The absorption would cause an error in any estimation of the absorption due to BD in this region. Therefore, any calculations by Beer's law of the BD percentage, after heating which considered the absorption in the 1750 cm^{-1} region would be in error. The calculation would imply a larger percentage BD than actually existed.

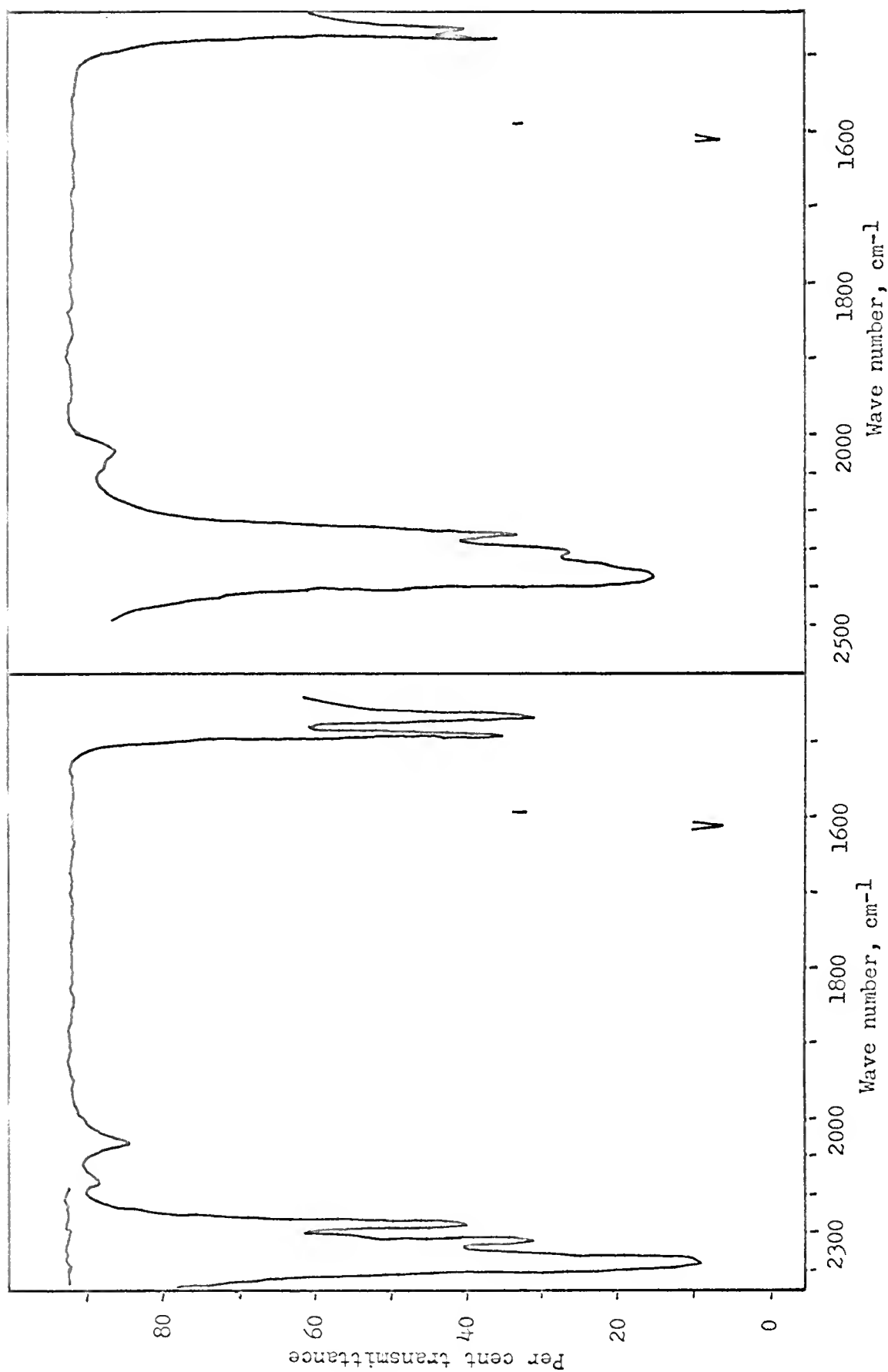


Fig. 17.--Infrared spectrum of $(\text{CH}_3)_3\text{NBH}_3$ after heating with D_2 for one hour.

Fig. 18.--Infrared spectrum of $(\text{CH}_3)_2\text{HNBH}_3$ after heating with D_2 for one hour.

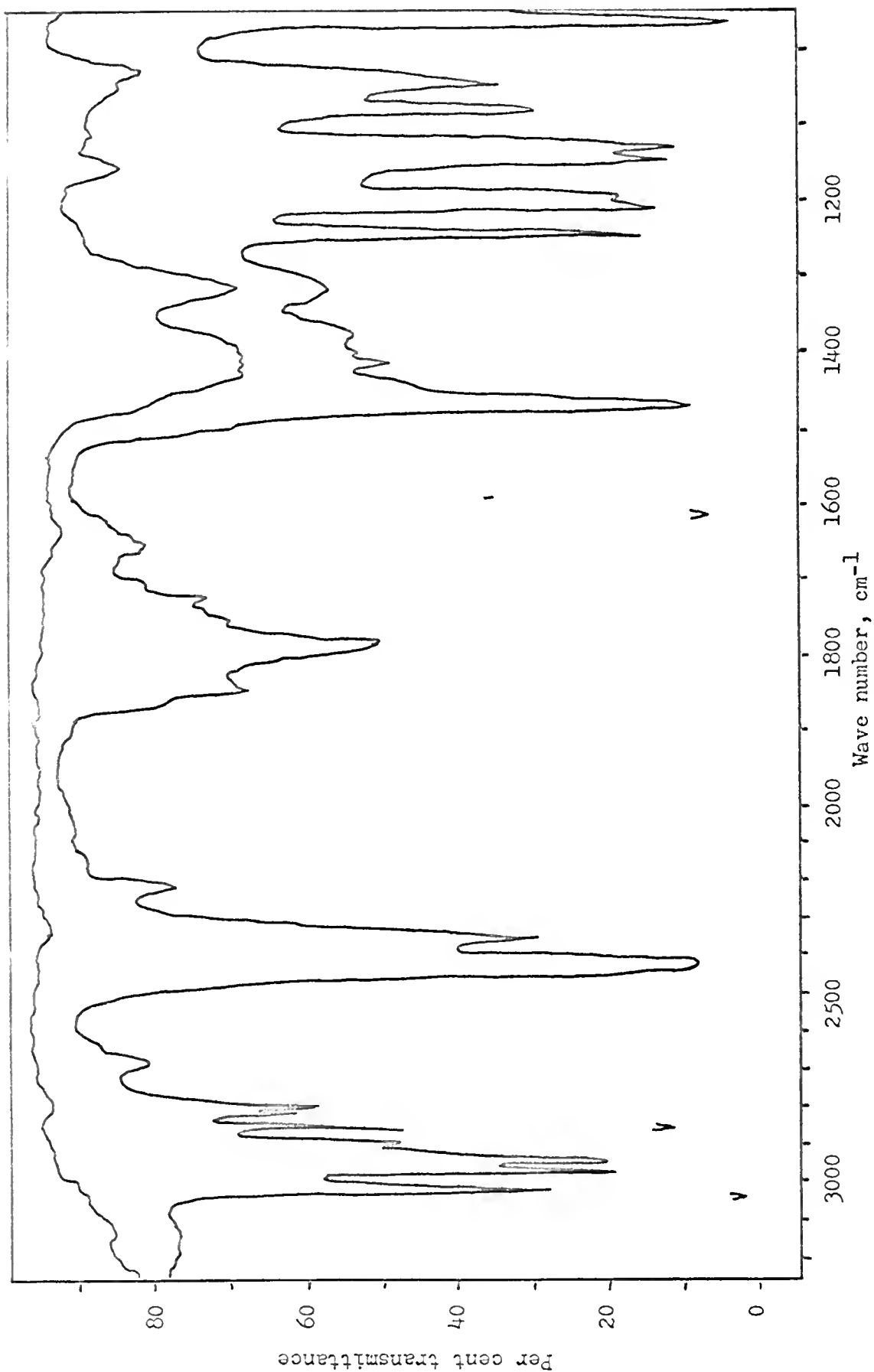


Fig. 19.---Infrared spectrum of $(\text{CH}_3)_2\text{HNBH}_3$ after heating with D_2 for twenty-four hours.

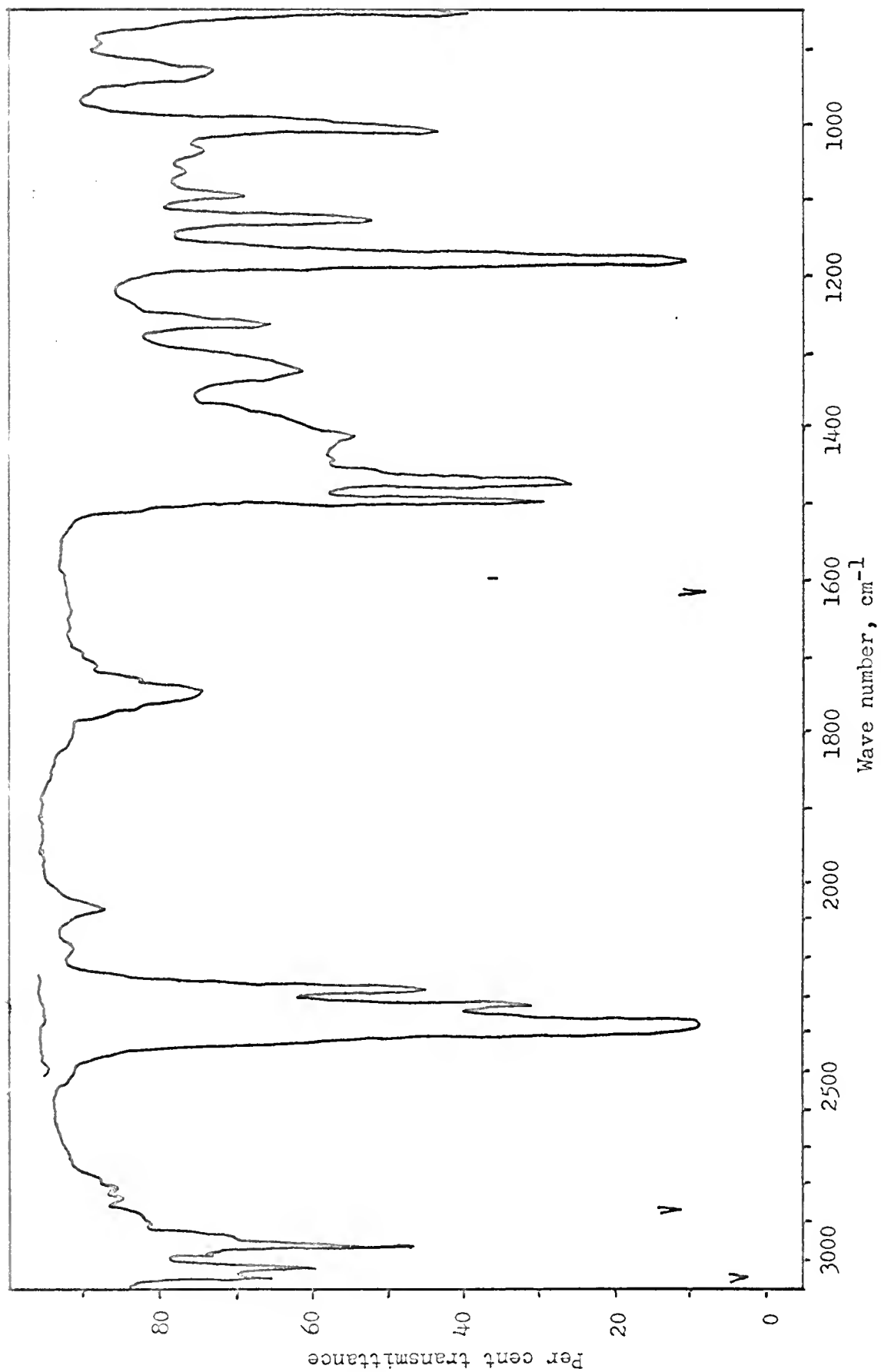


Fig. 20.--Infrared spectrum of $(\text{CH}_3)_3\text{NBH}_3$ after heating with D_2 for twenty-four hours.

The infrared spectrum of $(\text{CH}_3)_3\text{NBH}_3$ was unaffected by heating for twenty-four hours at 100° .

The data showed that exchange between dimethyl or trimethylamine borane and deuterium did not occur in one hour at 100° but that exchange did occur after twenty-four hours at 100° .

The data are summarized in Table 14.

III. Heating of $(\text{CH}_3)_2\text{DNBH}_3$ to determine if exchange occurred between ND and BH within the molecule.--N-deuterio-dimethylamine borane was heated at 100° for eleven hours in a sealed glass tube. The material was handled in the vacuum system or in the Dri-Lab controlled atmosphere box. The solid material was dissolved in spectral grade carbon tetrachloride and an infrared spectrum (Figure 3) obtained. This spectrum was compared to a spectrum of an unheated sample of $(\text{CH}_3)_2\text{DNBH}_3$ (Figure 2).

Beer's law was used to calculate the concentration of compound containing NH, ND, BH, and BD using the CH deformation peak as the internal reference (see Table 3). The spectra (Figures 2 and 3) showed an enrichment in the percentage of deuterium contained in the unreacted material, and a decrease in the percentage of hydrogen-containing material. The concentration of NH containing compounds decreased from 22 per cent to 15 per cent, ND increased from

TABLE 14

REACTION OF $(\text{CH}_3)_2\text{HNBH}_3$ AND $(\text{CH}_3)_3\text{NBH}_3$ WITH D_2

| Compound/mmoles | Reaction Time | Reaction Temperature | IR Spectrum | Mass Spectrum |
|---|---------------|----------------------|-------------------------------------|---------------|
| $(\text{CH}_3)_2\text{HNBH}_3 + \text{D}_2$ | 1 hr. | 100° | No change | No HD |
| 10.2 0.43 | | | | |
| $(\text{CH}_3)_2\text{HNBH}_3 + \text{D}_2$ | 24 hrs. | 100° | BD | |
| 1.30 0.51 | | | | |
| $(\text{CH}_3)_2\text{HNBH}_3$ | 34 hrs. | 100° | Absorption at 1750 cm^{-1} | |
| $(\text{CH}_3)_3\text{NBH}_3 + \text{D}_2$ | 1 hr. | 100° | No change | No HD |
| 9.89 0.32 | | | | |
| $(\text{CH}_3)_3\text{NBH}_3 + \text{D}_2$ | 24 hrs. | 100° | BD | |
| 1.31 0.50 | | | | |
| $(\text{CH}_3)_3\text{NBH}_3$ | 24 hrs. | 100° | No change | |

78 per cent to 85 per cent, BH decreased from 97 per cent to 92 per cent and BD increased from 3 per cent to 8 per cent when the compound was heated. During heating, dimethylaminoborane was formed, which had an absorption peak in the same region (1750 cm^{-1}) as the BD absorption. Therefore, the absorption peak at 1750 cm^{-1} in the spectrum of $(\text{CH}_3)_2\text{DNBH}_3$, after heating, could not be attributed solely to BD containing compounds, and the calculation of 8 per cent BD was an over-estimate. Any calculations or quantitative considerations of this 8 per cent BD would be questionable.

IV. Heating of $(\text{CH}_3)_2\text{DNBH}_3$ and $(\text{CH}_3)_2\text{HNBD}_3$ to determine if amine exchange occurred.---Dimethylamine borane- d_3 and N-deuterodimethylamine borane were sublimed into a tube equipped with a capillary break-off tip, and the glass was sealed. Duplicate tubes were heated at 100° for twenty-four hours.

The non-condensable product was removed and analyzed in the mass spectrometer (see Table 13). The solid products also were analyzed in the mass spectrometer (Figure 21).

The experiment was done in duplicate. In neither case did the mass spectra show a peak at the mass to charge ratio of 63. The peak at this m/e would occur only if the completely deuterated compound were present in the solid material. If amine exchange occurred, then this peak would

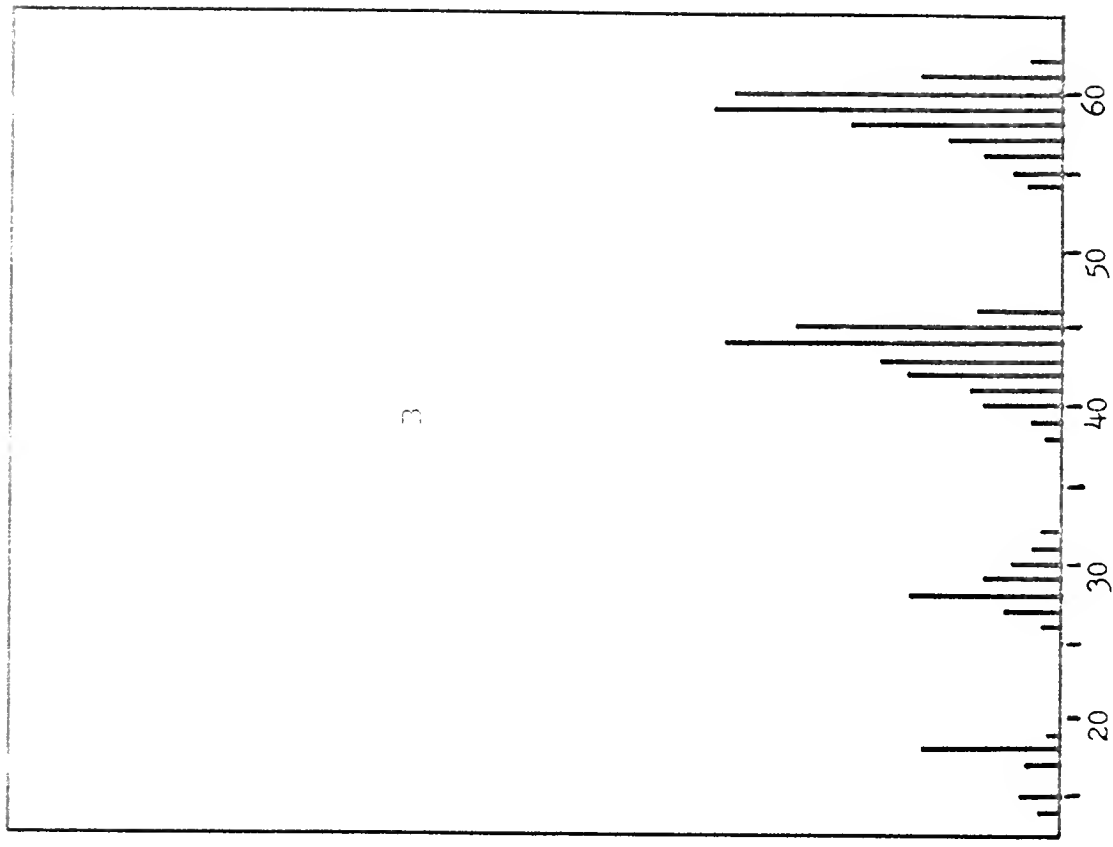
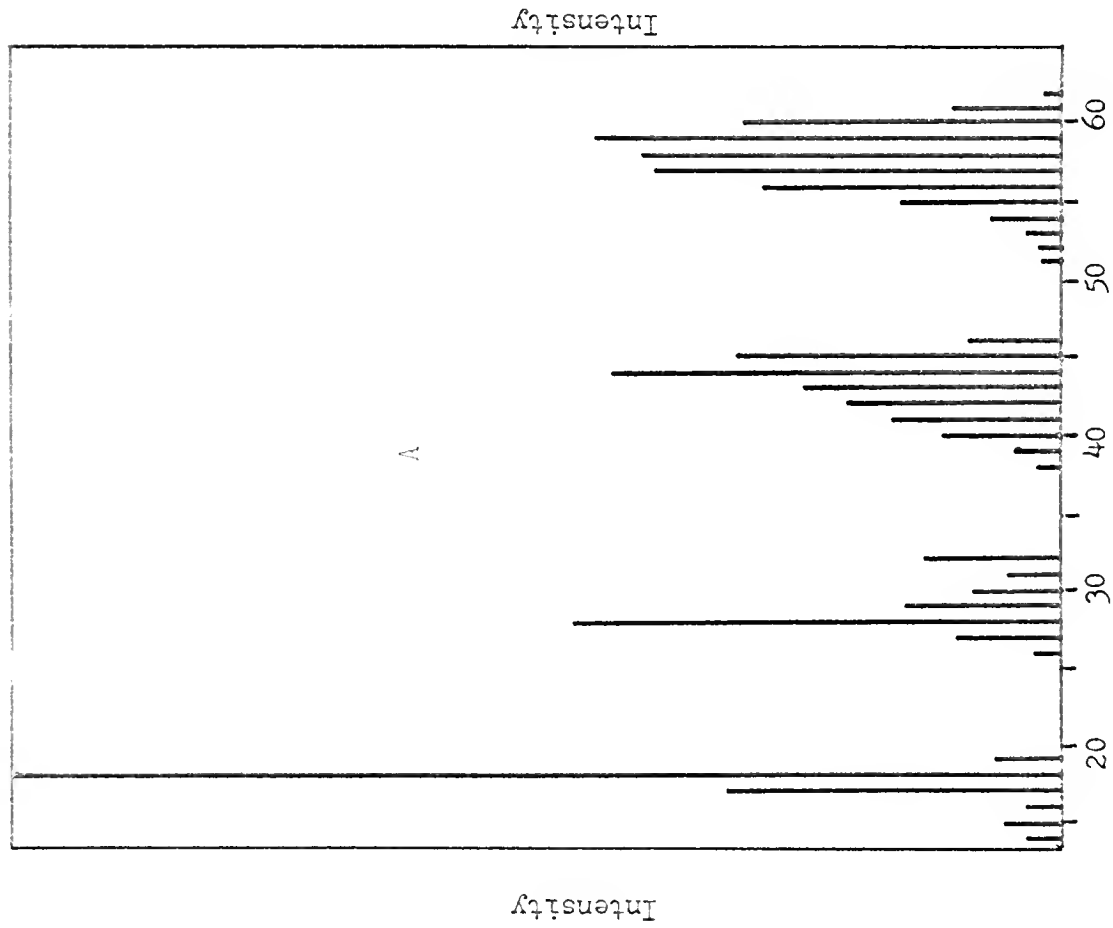


Fig. 21.--Mass spectrum at 70 ev after heating $(\text{CH}_3)_2\text{DNBH}_3$ and $(\text{CH}_3)_2\text{HNBBD}_3$ for twenty-four hours. (A) and (B) duplicate experiments.

be present; otherwise, the highest mass to charge ratio would be 62, the parent ion peak for $(\text{CH}_3)_2\text{HNBD}_3$. Therefore, amine exchange does not occur under the reaction conditions.

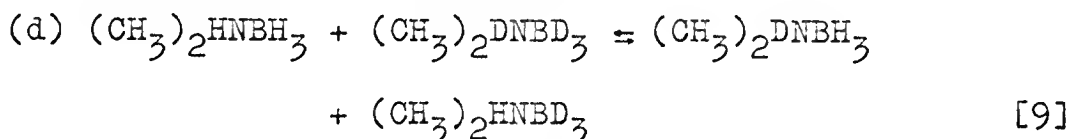
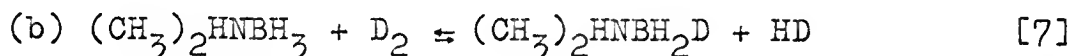
In the mass spectrum for $(\text{CH}_3)_2\text{HNBD}_3$, the ratio of the intensities of peak 61:62 was 7.9. The mass spectra, taken on the solid material after heating, contained a ratio of the peak intensities of 61:62 of 5.4 and 5.8 for the two experiments. In the recorded spectra, the peak at m/e of 62 was a shoulder on the peak at m/e of 61. The same base line was used to get both peak heights. This may not be the actual height of peak 62, but it may actually be less intense than measured, which would tend to bring the ratio of 61:62 more into line with that for the spectrum of $(\text{CH}_3)_2\text{HNBD}_3$.

DISCUSSION OF RESULTS

Possibility of hydrogen-deuterium exchange

Every isotope study must be thoroughly checked to make sure that an exchange process does not vitiate the conclusions. Exchange between hydrogen and deuterium, either in the gas phase or when bonded to other atoms within a molecule, could invalidate the experiment. Therefore, it becomes of primary importance to ascertain if any exchange reactions could occur under the experimental conditions. Even a kinetic isotope effect in the hydrogen elimination reaction would cause enrichment in the unreacted compounds of the less reactive isotope, and thus affect the measured ratio of $H_2:HD:D_2$ from a long term reaction. Therefore, the critical experiments to determine the isotope effect were run for only 1 to 2 per cent hydrogen elimination to avoid this possibility.

There are five processes by which isotopic interchange could occur:



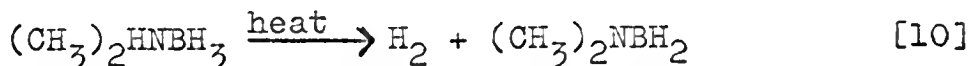
- (e) Exchange between reactants prior to amineborane formation. Each of these possibilities was examined experimentally.

The mass spectrum of a mixture of D_2 and H_2 with mercury vapor, heated for twenty-four hours at 100° , did not contain a peak at m/e of 3. Therefore, exchange reaction [6], even over mercury metal, did not occur.

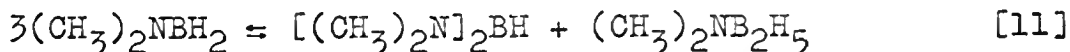
Dimethylamine borane and trimethylamine borane were heated with deuterium gas to determine if exchange occurred. After one hour at 100° , neither $(CH_3)_2HNBH_3$ or $(CH_3)_3NBH_3$ had exchanged with the D_2 gas. A mass spectrum of the gas from the reaction tube showed no HD, and the infrared spectrum of the solid materials showed no BD absorptions in the $1750-1800\text{ cm}^{-1}$ region.

However, after twenty-four hours at 100° , both $(CH_3)_2HNBH_3$ and $(CH_3)_3NBH_3$ had exchanged to some extent with the D_2 gas, since their infrared spectra showed BD absorptions in both instances.

The reaction products when dimethylamine borane was heated were hydrogen gas and dimethylaminoborane, according to the equation:



At 100° , the dimethylaminoborane will disproportionate (7) according to the equation:



Noeth (31) has reported that $(\text{CH}_3)_4\text{N}_2 \cdot 2\text{BH}_3$ will give $(\text{CH}_3)_2\text{NBH}_2$ and $(\text{CH}_3)_2\text{HNBH}_3$ when heated, and at 100° the principal product was $(\text{CH}_3)_2\text{NBH}_2$ and H_2 with some $[(\text{CH}_3)_2\text{N}]_2\text{BH}$ and $(\text{CH}_3)_2\text{NB}_2\text{H}_5$ being produced. Therefore, under the experimental conditions, the reaction products would not be just hydrogen and the aminoborane, but a more complicated mixture of compounds. Since aminodiborane is known (6) to exchange with deuterium gas, the argument could be made that it was this species or possibly the aminoborane which was exchanging with the deuterium gas and not the amine borane. But, the BH bonds in trimethylamine borane exchanged with deuterium gas under the same conditions. Therefore, it is not unlikely that exchange also occurred between dimethylamine borane and D_2 gas.

Deuterium gas has been reported to exchange also with diborane (6,12,37) and with the BH bonds in borazine (10).

From the experimental data, it can be concluded that exchange between deuterium gas and dimethyl or trimethylamine borane did not occur to a measurable extent in one hour at 100° , but that it did occur in twenty-four hours at 100° . This result must be considered in the interpretation of the experimental results.

The intramolecular exchange (equation [8]) did not occur when $(\text{CH}_3)_2\text{DNBH}_3$ was heated. Since the starting material contained some NH and BD bonds, the change in

relative concentrations in the infrared spectra, on heating, had to be calculated using Beer's law. The change in NH containing compound gave the more accurate results^a and indicated an enrichment of the deuterium containing compound in the unreacted material. The enrichment in ND bonds, in the material remaining after heating, implied that the NH bonds were lost much more readily. A relative change in the moles of NH to the moles of ND can be calculated from the spectral data. If one considered the total moles of dimethylamineborane, a , to be the sum of the moles of NH and ND, then before heating there were $0.22a$ moles of NH and $0.78a$ moles of ND. Assuming that the reaction was 30 per cent complete^b according to equation [10], then $0.30a$ total moles of both NH and ND reacted. After heating, the moles of NH were $(0.15)(1.00a - 0.30a)$ which was $0.105a$ and the moles of ND were $(0.85)(1.00a - 0.30a)$ which was $0.60a$. This corresponded to a decrease in moles of NH of $0.115a$ or 52.3 per cent and in moles of ND of $0.18a$ or 23.1 per cent. These calculations indicate the following:

(1) A hydrogen atom was eliminated 2.3 times more readily than a deuterium atom from the nitrogen.

(2) There was an increase in concentration of the deuterium-containing compound in the unreacted material.

^aSee page 16.

^bThis figure should be reasonably accurate considering the data in Table 12.

(3) Exchange between the ND and BH was not occurring to any significant extent during the reaction time. Otherwise, a greater decrease in ND would be expected and less of a decrease or even an increase in NH would be expected since there were 3 BH bonds per ND bond available for exchange in the original molecule.

The analogous calculation using the BD or BH absorptions would contain too large an error to be meaningful. Since ND and BH absorb in the same region, the BH absorption could not be used for the calculation. The BD absorption could be used, but to do so the following assumptions must be made:

(1) The absorptivities ratio of BH:CH is the same as that for BD:CH.

(2) The absorptivities of BH:CH in $(\text{CH}_3)_2\text{HNBH}_3$ is the same as that for BH:CH in $(\text{CH}_3)_2\text{NBH}_2$.

The second assumption was checked by heating $(\text{CH}_3)_2\text{HNBH}_3$ for thirty-four hours at 100° and then subliming out the most volatile portion of the reaction mixture. The infrared spectrum gave a ratio of absorptivity of BH:CH of 1.30 compared to that of 1.90 for $(\text{CH}_3)_2\text{HNBH}_3$. The lower value for the absorptivity ratio would cause an under-estimation of the amount of BH compound actually present if the value of 1.90 were used in the calculation. But, the

most significant point in this spectrum was an absorption at 1750 cm^{-1} . This absorption meant that a reaction product also absorbed in the same region as the BD vibration. Thus, an over-estimation would be made of the amount of BD containing material in an infrared spectrum after the compound was heated; the 8 per cent BD calculated from the spectrum after heating was probably much greater than the actual amount of BD.

Therefore, the experiment indicated that any intramolecular exchange between hydrogen and deuterium on heating was insignificant.

To determine whether amine exchange occurred between the amine borane molecules, N-deuterodimethylamine borane and dimethylamine borane- d_3 were heated at 100° for twenty-four hours. A mass spectrum of the solid materials did not contain a peak at m/e 63 which would be present if amine exchange had occurred to form N-deuterodimethylamine borane- d_3 . The mass spectrum did show an intense peak at m/e 61 which had a shoulder at m/e 62. If $(\text{CH}_3)_2\text{DNBD}_3$ had been present a low intensity peak at m/e 63 and a more intense peak at m/e 62 would have been expected. The intensity of the peak at m/e 62 did not increase, therefore no amine exchange took place. Moreover, its intensity could be fully accounted for by the presence of unreacted starting material. Therefore it was concluded on this basis that amine exchange did not occur.

However, the possibility of exchange between the gaseous elimination products and the dimethylamine boranes could account for the absence of the completely deuterated amine borane. Even if amine exchange occurred to give $(\text{CH}_3)_2\text{DNBD}_3$, a subsequent reaction with H_2 could conceivably have reduced the parent mass peak to an undetectable level. Thus, the above conclusion is open to some doubt.

The failure to prepare $(\text{CH}_3)_2\text{DNBH}_3$ and $(\text{CH}_3)_2\text{HNBD}_3$ in which there was not also an impurity of BD or ND bonds implied that an exchange reaction was occurring before adduct formation. The only other method to produce the impurity would be an intramolecular exchange in the adduct, but experimental evidence discounted this possibility even when the adduct was heated.

The compounds were prepared by condensing diborane and excess dimethylamine together and warming to -78° to form the adduct. An exchange reaction must have occurred at a rate comparable to the rate of adduct formations at this temperature. Dahl and Schaeffer (10) have reported that N-deuterodiethylamine exchanged with the BH bonds in borazine at -30° within three minutes. Since the ND bond in diethylamine exchanges with the BH bond in borazine, it would be reasonable to expect that a NH bond in a secondary amine could exchange with a BH bond in diborane. The infrared analysis of the dimethylamine boranes, prepared

from the amine and diborane, seemed to indicate that this exchange did occur to some extent.

The preparation of $(\text{CH}_3)_2\text{DNBH}_3$ from $(\text{CH}_3)_2\text{ND}_2\text{Cl}$ and excess LiBH_4 contained even more BD bonds according to the infrared spectrum than were present in the compound prepared from amine and diborane. The infrared spectrum of $(\text{CH}_3)_2\text{DNBH}_3$ implied that 72.8 per cent ND bonds and 13.2 per cent BD bonds were present in the compound. The calculation was made from Beer's law, using the CH deformation at 1475 cm^{-1} as the internal standard. The comparison of 13.2 per cent BD bonds to 27.2 per cent NH bonds indicated that an exchange reaction occurred prior to the reaction to produce the amine borane. Otherwise, the per cent BD bonds should be equal to the per cent NH bonds if the exchange occurred after the amine borane was formed. If the exchange reaction did occur before amine borane formation, as the data implied, then the unreacted LiBH_4 should have contained some BD bonds.

N-deuterodimethylamine borane, prepared from the amine and diborane, contained 3 per cent BD as compared to 13.2 per cent in the compound prepared from $(\text{CH}_3)_2\text{ND}_2\text{Cl}$ and LiBH_4 . These data indicated that the exchange reaction between $(\text{CH}_3)_2\text{ND}_2^+$ and BH_4^- occurred to a greater extent before adduct formation than was observed for the amine diborane reaction.

Heating mixtures of dimethylamine boranes containing various distributions of hydrogen isotopes for one hour

In order to determine if the kinetic isotope effect in the elimination reaction could be attributed to the nitrogen or boron-bonded hydrogen isotope, mixtures of dimethylamine boranes were heated at 100° for one hour. A reaction time of one hour was used to minimize the reaction extent so that the observed product compositions could be related unequivocally to a known isotopic distribution in the reactants. In each mixture, either the boron or nitrogen bond was one hydrogen isotope, and the other hydrogen bonds in that molecule and in the other molecules were the other hydrogen isotope; for example, one mixture was $(\text{CH}_3)\text{HNBD}_3$ and $(\text{CH}_3)\text{DNBD}_3$. The isotopic distribution was varied to determine if a NH or a ND bond was eliminated more readily or whether a BH bond reacted more readily than a BD bond.

The results in Table 13 show the following: (1) If one molecule contained a NH bond, and the rest of the hydrogen in the system was the deuterium isotope, then the principal product was HD, the ratio of $\text{H}_2:\text{HD}:\text{D}_2$ being 0.15:1.00:0.39. (2) If one molecule contained ND bonds, and the rest being the hydrogen isotope, then the principal product was H_2 , the ratio of $\text{H}_2:\text{HD}:\text{D}_2$ being 4.75:1.00:0.0. (3) If one molecule contained BH bonds, and the rest being

the deuterium isotope, then the principal product was HD, the ratio of $H_2:HD:D_2$ being 0.52:1.00:0.67. (4) If one molecule contained BD bonds, and the rest being the hydrogen isotope, then the principal product was H_2 , the ratio of $H_2:HD:D_2$ being 1.32:1.00:0.05.

The data implied that a hydrogen atom was eliminated more readily than a deuterium atom since in each instance the primary product was either H_2 or HD and not D_2 , even in the cases where there was only one NH or BH bond in the system. The data were consistent with a BD bond being eliminated more readily than a ND bond. In the experiments which compare these two bonds, the $H_2:HD$ ratio was 4.75:1.00 for the ND case and 1.32:1.00 for the BD case. This implied that HD was eliminated between a BD bond and a NH bond approximately 3.6 times faster than between a ND bond and a BH bond. The HD: D_2 ratio of 2.56, when $(CH_3)_2DNBD_3$ and $(CH_3)_2HNBD_3$ were heated, compared to the HD: D_2 ratio of 1.39, when $(CH_3)_2DNBD_3$ and $(CH_3)_2DNBH_3$ were heated, indicated that HD was eliminated between a BH bond and a ND bond 1.84 times faster than between a NH bond and a BD bond.

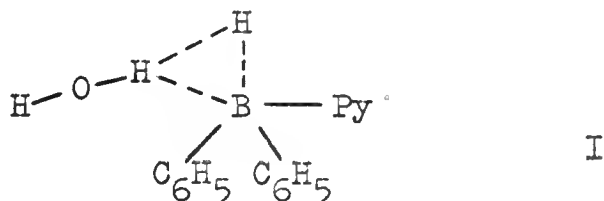
The HD: D_2 ratio of 2.56, when $(CH_3)_2DNBD_3$ and $(CH_3)_2HNBD_3$ were heated, and the $H_2:HD$ ratio of 4.75, when $(CH_3)_2DNBH_3$ and $(CH_3)_2HNBH_3$ were heated, indicated a large kinetic isotope effect to be occurring when the hydrogen isotope bonded to the nitrogen atom was varied. Thus, the

ratio of the rate constants for the nitrogen atom eliminating a hydrogen or deuterium atom $\left(\frac{k_{\text{NH}}}{k_{\text{ND}}}\right)$ experimentally determined, varied between 2.7 and 4.8. Edwards (13) has predicted a ratio of the rate constants for the bond breaking process involving NH and ND bonds $\left(\frac{k_{\text{NH}}}{k_{\text{ND}}}\right)$ of 8.5. The average experimental isotope effect for the $\left(\frac{k_{\text{NH}}}{k_{\text{ND}}}\right)$ of 3.8 was less than the predicted ratio of 8.5. This implied that there was considerable, but not complete, loss of the NH stretching vibration in the activated complex.

The HD:D₂ ratio of 1.39, when (CH₃)₂DNBD₃ and (CH₃)₂DNBH₃ were heated, and the H₂:HD ratio of 1.32, when (CH₃)₂HNBD₃ and (CH₃)₂HNBH₃ were heated, indicated a small kinetic isotope effect to be present when the hydrogen isotope bonded to boron was varied. Thus, the ratio of the rate constants for the boron atom eliminating a hydrogen or deuterium atom $\left(\frac{k_{\text{BH}}}{k_{\text{BD}}}\right)$, experimentally determined, was 1.3 to 1.4. Hawthorne and Lewis (17) calculated the ratio of $\left(\frac{k_{\text{BH}}}{k_{\text{BD}}}\right)$ to be 4.2 for the expected effect of isotopic substitution on boron from the loss of the BH stretching vibration at 2300 cm⁻¹. The observed isotope effect was much less than that predicted, implying that there was only a small loss of the BH stretching vibration in the activated complex.

The maximum isotope effect would be obtained when the bond to hydrogen or to deuterium was essentially completely cleaved in the activated complex, and the isotope effect would decrease with increasing bonding in the activated complex (44). Therefore, the isotope effects observed should allow some predictions about a possible configuration of the activated complex in the hydrogen elimination reaction. The larger effect when ND was substituted for NH than when BD was substituted for BH predicts that the NH(ND) bond was more affected in the activated complex than was the BH(BD) bond. Hawthorne (17) has reported a similar situation in the hydrolysis of pyridine diphenylborane with water or deuterium oxide in acetonitrile solution. The reaction was found to be first order in both pyridine diphenylborane and water, and a primary kinetic isotope effect was determined. The ratio of the rate constants $\left(\frac{k_{\text{OH}}}{k_{\text{OD}}} \right)$ of 6.90, when deuterium oxide was substituted for water, was nearly as large as that predicted for a complete loss of the OH stretching vibration in the activated complex of 9.9. The ratio of the rate constants $\left(\frac{k_{\text{BH}}}{k_{\text{BD}}} \right)$ of 1.52 observed on isotopic substitution on boron was much less than the predicted $\left(\frac{k_{\text{BH}}}{k_{\text{BD}}} \right)$ of 4.2 for complete loss of the BH stretching vibration in the activated complex.

Hawthorne (17) proposed the transition state (I) for the BH bond hydrolysis and suggested that this type of non-linear transition state may be general for hydride transfer.



The similarity between the isotope effect observed by Hawthorne, and that observed here in the hydrogen elimination reaction of dimethylamine borane, suggests that the reactions might be occurring through a similar activated complex. Namely, that the activated complex was not a linear configuration involving NH and BH bonds but that the NH bond was stretched more along the bond axis than was the BH bond, in a manner analogous to that for the OH and BH bonds in I.

These data must be interpreted in the light of possible exchange reactions occurring faster than the elimination reaction. Since hydrogen and deuterium gas did not exchange when heated for 24 hours at 100°, this possibility could be discounted. If amine exchange between boranes occurred, there would be no net change in the systems, so this would not cause any difficulties. Deuterium

gas when heated at 100° for one hour with dimethylamine borane did not affect the infrared spectrum of the solid material. Therefore, it may be concluded that no isotope exchange reactions occurred during one hour at 100°, and that the data were not subject to any uncertainties due to exchange.

The starting materials were not as pure in their isotopic distribution as would be necessary to determine a precise kinetic isotope effect in the hydrogen elimination reaction. The infrared spectra showed the following:

(1) $(\text{CH}_3)_2\text{DNBH}_3$ contained 3 per cent BD bonds relative to the per cent CH bonds.

(2) $(\text{CH}_3)_2\text{HNBD}_3$ contained 7 per cent ND bonds relative to the per cent CH bonds.

(3) $(\text{CH}_3)_2\text{DNBH}_3$ contained 13 per cent BD bonds relative to the per cent CH bonds.^a (Prepared from $(\text{CH}_3)_2\text{ND}_2^+$ and BH_4^-).

Compounds (1) and (2) were prepared by condensing dimethylamine and diborane together and forming the adduct at -78°. Compound (3) was prepared from $(\text{CH}_3)_2\text{ND}_2^+$ and BH_4^- . In each instance some exchange must have occurred before the reaction producing the amine borane adduct.

^aThis compound was not used in any of the hydrogen elimination experiments.

The presence of isotopic impurities introduced during synthesis would account for the D_2 produced when $(CH_3)_2HNBD_3$ and $(CH_3)_2HNBH_3$ were heated and for the H_2 produced on heating $(CH_3)_2HNBD_3$ with $(CH_3)_2DNBD_3$ and $(CH_3)_2DNBH_3$ with $(CH_3)_2DNBD_3$.

The data from the one-hour heating experiments did not unequivocally distinguish between a unimolecular and a bimolecular reaction mechanism. But, the analogy to Hawthorne's work with the hydrolysis of pyridine diphenylborane (17) and the large percentages of HD obtained in each case does favor a bimolecular reaction. However, the molecularity of the reaction was resolved by the experiment in which $(CH_3)_2DNBD_3$ and $(CH_3)_2HNBH_3$ were heated.

Heating mixtures of dimethylamine boranes containing various distributions of hydrogen isotopes for twenty-four hours

Dimethylamine borane and N-deuterodimethylamine borane- d_3 , in 1:1 molar ratio, were heated at 100° for twenty-four hours and the non-condensable products were analyzed in a mass spectrometer. If the hydrogen elimination reaction were unimolecular, then the gaseous product should contain H_2 , D_2 and perhaps some HD due to incomplete deuteration. If the reaction were bimolecular, the gaseous products should be H_2 , HD and D_2 in the ratio of 1:2:1, respectively, neglecting isotope effects.

The experimentally determined ratio of $H_2:HD:D_2$ was 3.8:4.3:1.0. The data implied that the reaction was bimolecular and that there was an isotope effect favoring H_2 eliminations in the reaction.

Dimethylamine borane- d_3 and N-deuterodimethylamine borane, in a 1:1 molar ratio, were heated for twenty-four hours at 100° and the non-condensable reaction products were analyzed in the mass spectrometer.^a If the reaction were unimolecular the gaseous product should be HD with the D_2 and H_2 due to incomplete deuteration. If the reaction were bimolecular, the gaseous products should be H_2 , HD and D_2 in ratio of 1:2:1 neglecting isotope effects.

The gaseous products had a $H_2:HD:D_2$ ratio of 3.1:3.6:1.0. Since the gaseous products of the reaction contained more H_2 and D_2 than could be accounted for by incomplete deuteration, the reaction must have been bimolecular. The data were in close agreement with the previous results and indicated that it made no difference whether the deuterium atoms were all in one molecule or partly on the nitrogen in one molecule and partly on the boron in the other molecule. The results in both cases gave the same percentages of H_2 , HD and D_2 in the gaseous product.

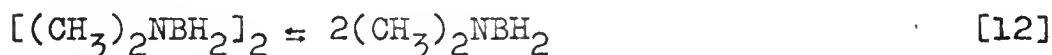
The total deuterium percentage in each of the reaction systems, $(CH_3)_2HNBH_3 - (CH_3)_2DNBD_3$ and $(CH_3)_2DNBH_3 -$

^aFor mass spectral analysis of the solid reaction products see Figure 21.

$(\text{CH}_3)_2\text{HNBd}_3$, was almost the same. From the infrared spectra, the system $(\text{CH}_3)_2\text{DNBH}_3 - (\text{CH}_3)_2\text{HNBd}_3$ contained 47.4 per cent deuterium bonds and from the pyrolysis products of the diborane- d_6 , the system $(\text{CH}_3)_2\text{HNBH}_3 - (\text{CH}_3)_2\text{DNBD}_3$ contained a minimum of 45.4 per cent deuterium bonds. Therefore, it was not surprising that under the same conditions, if the reaction were bimolecular or if an equilibrium reaction were established, for these two systems to give the same ratio of $\text{H}_2:\text{HD}:\text{D}_2$ in the gaseous elimination products.

However, the interpretation of these results was made questionable by the possibility that exchange occurred during the reaction between deuterium and the reactants or other reaction products. Some exchange did occur between dimethylamine borane and deuterium gas on heating for twenty-four hours at 100° , the same conditions as in these experiments. In order for the two experiments to have had the same ratio of $\text{H}_2:\text{HD}:\text{D}_2$ in the gas phase with exchange occurring between the gases and other compounds in the system, the reaction mixtures in each experiment must have reached the same equilibrium.

Equilibrium would have been established according to the following equations for the boron containing reaction products (7).





Burg (6) reported that the aminodiborane in the presence of excess D_2 after seventy-four hours at 100° was found to be 65 per cent deuterated. In experiments using D_2 gas to deuterate a compound, a large excess of D_2 gas and long reaction times were used to be sure an equilibrium was established. In the hydrogen elimination reaction of $(\text{CH}_3)_2\text{DNBD}_3$ and $(\text{CH}_3)_2\text{HNBH}_3$, the per cent reaction was 31.3 per cent. Therefore, of the original 1.59 mmoles of amine borane, there remained 1.09 mmoles unreacted amine borane, with 0.50 mmoles of gas and 0.50 mmoles of amino-borane produced. The 0.50 mmoles of gas contained 0.06 mmoles D_2 , 0.22 mmoles HD and 0.20 mmoles H_2 . If an exchange reaction were occurring between the gaseous hydrogen isotopes and the boron-nitrogen compounds, then the ratio of $\text{H}_2:\text{D}_2$ in the gaseous product should be the same as the ratio of $\text{H}_2:\text{D}_2$ over any other catalytic system. Essentially the boron-nitrogen compounds would be serving as a catalyst for the hydrogen-deuterium exchange reaction, $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$. Considering the total moles of gas to be A, then the amount of hydrogen gas available in the $(\text{CH}_3)_2\text{HNBH}_3 - (\text{CH}_3)_2\text{DNBD}_3$ system would be 0.26A moles and of deuterium would be 0.24A moles. Using the equilibrium constant, 3.48 at 400°K , calculated by Urey (42) for the deuterium exchange, the moles of HD were calculated to be 0.20A; and thus, the

concentration at equilibrium of H_2 would be 0.08A and of D_2 was 0.06A. The ratio of $H_2:D_2$ at equilibrium would therefore be 1.33. The observed ratio of $H_2:D_2$ was 3.33, implying that the gaseous products were not at equilibrium for the exchange reaction.

If an exchange reaction were occurring between the gaseous hydrogen isotopes and the boron-nitrogen compounds, then a consideration of the difference in zero-point energy between a BH and a BD bond compared to the difference in H_2 and D_2 bonds should give an indication of the thermodynamically favored reaction.

For two isotopes in an otherwise identical bond, the difference between the two zero-points of energy is given by $E = \frac{1}{2}h(\nu - \nu')$, where ν and ν' refer to bonds containing the lighter and heavier isotopes X and X', respectively. The difference in ν_{BH} and ν_{BD} calculated from only the stretching vibrations at 2350 cm^{-1} (BH) and 1875 cm^{-1} (BD) was 1.36 kcal/mole, and the difference in ν_{HH} and ν_{DD} calculated from the frequencies for the fundamental vibration transitions (1) of 4159 cm^{-1} (HH) and 2990 cm^{-1} (DD) was 3.34 kcal/mole. Thus, a comparison of the differences in zero-point energies indicated that the reaction to produce D_2 would be thermodynamically the most favored and the gas phase should be enriched in D_2 . This was contrary to the observed kinetic isotope effect and the observed ratio

of 41.3 per cent H_2 :47.7 per cent HD:11.0 per cent D_2 in the gaseous product.

Therefore, it does not appear likely that the exchange reaction between H_2 , HD or D_2 and the amine boranes or aminoboranes had reached equilibrium in twenty-four hours at 100° . The exchange reaction, thus, has only a secondary effect on the eliminated gases and the reaction must be bimolecular as was inferred by the experiments on heating the dimethylamine boranes for one hour.

CONCLUSION

The reaction of dimethylamine borane to eliminate hydrogen was bimolecular and a kinetic isotope effect occurred during the elimination of hydrogen. The data showed that a hydrogen atom was eliminated faster than a deuterium atom and that a BD bond reacted more readily than a ND bond.

The ease and speed of deuterium and hydrogen atoms exchange limits many of the possible experiments which might be used to elucidate the behavior of the dimethylamine borane system on heating, and in studying the kinetic isotope effect in the reactions of the amine boranes. More work needs to be done to establish the conditions and possibly the rates of the deuterium-hydrogen exchange reaction in the BN containing compounds. A case in point being R. E. Davis' report (11) that the rate of deuterium exchange in acidic D_2O with trimethylamine borane was much more rapid than the hydrolysis reaction. In this work, evidence was presented that for N-deuterodimethylamine borane- d_3 , the rate of exchange with acidic H_2O was approximately equal or only slightly faster than the rate of hydrolysis. This inferred a possible order of magnitude for the rate of the exchange reaction.

The unsuccessful attempts to prepare $(\text{CH}_3)_2\text{DNBH}_3$ or $(\text{CH}_3)_2\text{HNBD}_3$ with only the isotopic distribution indicated, suggested that before any experiments can be successfully designed for these compounds, more information about hydrogen-deuterium exchange reactions of boron-nitrogen compounds would be necessary. These exchange reactions, or merely the possibility of such, means that any experiments with isotopically labelled amine boranes must be examined critically to make sure that it is not an exchange reaction which gave the measured results. In this work, the hydrogen elimination reaction of dimethylamine borane has been considered in view of the possibility of an exchange reaction. The evidence strongly inferred a bimolecular reaction.

SUMMARY

To determine the mechanism of the dehydrogenation of dimethylamine borane, $(\text{CH}_3)_2\text{HNBH}_3$, the following compounds were prepared.

N-deuterodimethylamine borane- d_3 , $(\text{CH}_3)_2\text{DNBD}_3$, N-deuterodimethylamine borane, $(\text{CH}_3)_2\text{DNBH}_3$ and dimethylamine borane- d_3 , $(\text{CH}_3)_2\text{HNBD}_3$ were prepared by condensing together the appropriate isotopically labelled diborane and dimethylamine. Deuterated diborane was prepared either by displacement from $(\text{CH}_3)_3\text{NBD}_3$ with $\text{BF}_3(\text{g})$ or by reaction of NaBD_4 with $\text{BF}_3(\text{g})$. The $(\text{CH}_3)_3\text{NBD}_3$ was prepared by an exchange reaction between acidic D_2O and $(\text{CH}_3)_3\text{NBH}_3$. N-deuterodimethylamine was prepared by hydrolysis of $\text{LiN}(\text{CH}_3)_2$ with D_2O . Lithium dimethylamide was prepared from n-butyl lithium and dimethylamine.

The following mixtures of compounds were heated for twenty-four hours at 100° : $(\text{CH}_3)_2\text{DNBD}_3$ and $(\text{CH}_3)_2\text{HNBH}_3$; $(\text{CH}_3)_2\text{DNBH}_3$ and $(\text{CH}_3)_2\text{HNBD}_3$.

The following mixtures were heated for one hour at 100° : $(\text{CH}_3)_2\text{DNBH}_3$ and $(\text{CH}_3)_2\text{HNBH}_3$; $(\text{CH}_3)_2\text{HNBD}_3$ and $(\text{CH}_3)_2\text{DNBD}_3$; $(\text{CH}_3)_2\text{HNBD}_3$ and $(\text{CH}_3)_2\text{HNBH}_3$; $(\text{CH}_3)_2\text{DNBH}_3$ and $(\text{CH}_3)_2\text{DNBD}_3$.

The results indicated that the dehydrogenation reaction was bimolecular and that a kinetic isotope effect occurred during the reaction, favoring the elimination of hydrogen rather than deuterium. The possibility of an isotopic exchange reaction occurring which could cast doubt on the results was considered and determined not to be significant in this work.

The larger isotope effect when deuterium was substituted for hydrogen on the nitrogen atom than on the boron atom indicated the presence of a non-linear activated complex in which the NH bond was more stretched along the bond axis than was the BH bond.

PART II. SYNTHESIS OF TRIMETHYLAMINE CHLOROBORANES

INTRODUCTION

Alkyl (or aryl) substitution on the boron atom has been done primarily on a boron atom in the three-coordinate state. Grignard reagents, organolithium reagents, and other organic-metallic reagents have been utilized in addition to disproportionation reactions between diborane and alkylboranes. A general review of these methods may be found in either W. Gerrard's Organic Chemistry of Boron (15) or H. C. Brown's Hydroboration (3).

Halogen substitution on the boron atom in the amine boranes has been accomplished using hydrogen halide gases (40,32), the halogens (32), or the trihaloboranes (32,36). The different halogen reagents reacted to different extents with the amine boranes.

Amine exchange can occur between the amine borane molecules and a free amine. The transamination reaction under certain circumstances has been also found (26) to give boronium ions containing two amines attached to the boron and the overall group having a positive charge.

Since amine boranes are known to be reducing agents toward aldehydes and ketones (22), as well as toward silver

(I) ions, it would be of interest to investigate what happened to the boron compound during these reactions. By proper choice of reactants and conditions, the redox reaction might be used as a means to substitute a group, or atom, into the boron compound.

In an attempt to obtain an x-ray diffraction pattern of trimethylamineborane, mercuric chloride was selected as the internal reference. The two solids were placed in a mortar and ground together. As the solids were ground, the color of the material turned gray. The color change implied that a reaction had occurred and the physical appearance indicated that mercury metal was being produced. Further study of this reaction showed that the chloroborane adducts were produced. The method proved to be a good preparative route to $(\text{CH}_3)_3\text{NBHCl}_2$.

These observations suggested a simple sequence of events. The two electrons gained by Hg(II) would most probably come from the hydridic BH bond. If the boron lost a hydride ion, the site formerly occupied by this atom could be occupied by a chloride ion from mercuric chloride. This would be possible if the BN bond remained intact and no other reactions occurred to degrade the molecule. Thus, this reaction sequence would give a simple route to boron-substituted amine boranes.

Using, as a working hypothesis, the idea that a metal ion in a high oxidation state can accept electrons from a BH bond to give H^+ (or H), the metal in a lower oxidation state, and a boron atom with an acceptor site which may be occupied by the strongest base in the reaction system, a variety of reactions may be considered. This method would be widely applicable and it could conceivably give many compounds which were previously difficult to prepare. The major practical limitations to this method would be unfavorable solubilities of the salts and difficulties in recovery of the products from the reaction mixture before further reactions could occur.

Other oxidizing agents considered were $(CH_3)_3NHCl$, SO_2Cl_2 , $SOCl_2$, $SbCl_5$, and $SbCl_3$. The order of reactivity of these compounds with trimethylamine borane was established. Evidence was found that the reactivity of the BH bond as a reducing agent decreased with increasing chloro substitution on the boron atom.

EXPERIMENTAL

Nomenclature

The compounds formed by the reaction of diborane and an amine have been named as amine adducts of borane or of substituted boranes. The following is a list of compounds considered in Part (II):

- trimethylamine borane, $(\text{CH}_3)_3\text{NBH}_3$;
- trimethylamine monochloroborane, $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$;
- trimethylamine dichloroborane, $(\text{CH}_3)_3\text{NBHCl}_2$;
- trimethylamine trichloroborane, $(\text{CH}_3)_3\text{NBCl}_3$.

Reagents and purification

Trimethylamine hydrochloride was obtained from Eastman Organic Chemicals and dried in a vacuum desiccator before use.

Trimethylamine trichloroborane was prepared from $\text{BCl}_3(\text{g})$ and $(\text{CH}_3)_3\text{N}(\text{g})$ and recrystallized from ethanol before use.

Antimony pentachloride was obtained from Allied Chemical Company and used without further purification.

Antimony trichloride was the Fisher certified reagent grade. It was sublimed under vacuum at 90° before use.

Mercuric chloride was the Fisher certified reagent grade. It was ground to a fine powder in a mortar and was used without further purification.

Trimethylamineborane was obtained from Callery Chemical Company. It was purified by vacuum sublimation from room temperature onto a glass cold finger at -78° .

Diethyl ether was the Fisher technical grade. It was dried over CaH_2 or "dri-Na" unless otherwise specified.

Anhydrous ether used was Fisher reagent chemical.

Carbon tetrachloride used in recrystallizations and extractions was the technical grade. It was used without further purification.

Ethyl alcohol used in extractions was 95 per cent pure and used without further purification.

Anhydrous hydrogen chloride was taken directly from a Matheson lecture cylinder.

Instruments

A 100 ml stainless steel autoclave was used. In certain experiments a removable glass liner was inserted into the autoclave to facilitate the removal of the reaction mixture.

A Wheelco Model 293 temperature controller with a Chromel-Alumel thermocouple was used to regulate the temperature of the upright autoclave furnace.

An all-glass vacuum system was used according to the standard technique (21); non-condensable gases were measured by transferring them into a calibrated volume with a Toepler pump.

Melting points were taken in capillary tubes in a stirred oil bath.

Solvents were removed either in a Rinco rotating evaporator or by using a water aspirator vacuum to evaporate the solvent.

All infrared spectra were taken as KBr pellets on a Beckman IR-10 Spectrophotometer.

Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Extraction of BN compounds from the reaction mixture

The first extraction of BN compounds was by filtering the reaction mixture. In this work, this solvent was diethyl ether. Then approximately an equal volume of ether was added to the solid residue, the mixture was stirred for five to ten minutes and then filtered again. The ether solutions usually still contained some Hg_2Cl_2 which came through the filters or which was produced in the filtrate due to a continuing reaction. Even fine porosity sintered glass filters did not prevent some Hg_2Cl_2 contamination in the filtrate.

Mercury metal was then added to the ether solution and the mixture shaken vigorously, precipitating a dense black material, most likely Hg_2Cl_2 and finely divided mercury.

The mixture was allowed to sit for two to three hours or longer before refiltering. The clear ether solution, thus obtained, was evaporated using a water aspirator vacuum. A white solid was left behind.

The white solid was recrystallized from hot CCl_4 . The material was dissolved in boiling CCl_4 , but it was not completely soluble. The hot solution was filtered and the filtrate cooled in a freezer compartment of a refrigerator. The cold CCl_4 was filtered to give the BN compounds. Next, the solvent was removed from the filtrate with a rotating evaporator. The material recovered from the filtrate was either recrystallized from a smaller portion of CCl_4 or was washed with cold CCl_4 . The latter usually proved to be sufficient to obtain a pure product.

The next extraction of the reaction residue was made using excess boiling CCl_4 .^a The CCl_4 extraction solution did not contain as much Hg(II) ion as the ether extraction solution judging from the amount of black precipitate

^aAt this point, a very strong odor of HCl was noted. The rest of the procedure was the same as for the ether extraction.

produced when mercury was added to the respective solutions. The filtrations had to be done on boiling solutions.

It was possible to distinguish the chloro adducts by their infrared spectra. Thus, infrared analysis of the extracted solids could be used to determine if the solids were pure compounds or to ascertain the identities of components in a mixture.

The solubilities of $(\text{CH}_3)_3\text{NBH}_3$, $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$, $(\text{CH}_3)_3\text{NBHCl}_2$, and $(\text{CH}_3)_3\text{NBCl}_3$ varied only slightly as more chlorine atoms were substituted for hydrogen atoms and decreased with progressive chlorine substitution. The solubility of $(\text{CH}_3)_3\text{NBH}_3$ and $(\text{CH}_3)_3\text{NBCl}_3$ differed widely enough that they could be easily separated. But if $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and $(\text{CH}_3)_3\text{NBHCl}_2$ were added to the mixture, the solvents used (diethyl ether, CCl_4 , ethanol or benzene) would not separate the compounds quantitatively. However, a final extraction with hot ethanol would have removed any $(\text{CH}_3)_3\text{NBCl}_3$ from the reaction residue if it were present.

Infrared spectral analysis

The infrared spectra of these compounds were sufficiently different that each adduct could be distinguished in a spectrum taken on a mixture of the adducts. Table 15 lists the infrared absorptions of the compounds. The most characteristic region of the spectrum was the $300\text{-}600\text{ cm}^{-1}$.

TABLE 15
INFRARED SPECTRA OF $(\text{CH}_3)_3\text{NBH}_3$ AND THE TRIMETHYLAMINE CHLOROBORANES

| $(\text{CH}_3)_3\text{NBH}_3$ | $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ | $(\text{CH}_3)_3\text{NBHCl}_2$ | $(\text{CH}_3)_3\text{NBCl}_3$ |
|------------------------------------|--|---------------------------------|------------------------------------|
| 3030-3010 cm^{-1} | 3040-3020 cm^{-1} | 3040-3020 cm^{-1} | 3050-3030 cm^{-1} |
| 2960 CH ν | 2960 CH ν | 2970 CH ν | 2970 CH ν |
| 2360 \leftrightarrow 2400, 2310 | 2440 \leftrightarrow 2420 | 2480 BH ν | |
| 2260-2290 BH ν | 2340 BH ν | | |
| 1485-1475 CH δ | 1485-1475 CH δ | 1490-1470-1455 CH δ | 1490-1465-1450 CH δ |
| 1410 | 1410 | 1410 | 1410 |
| 1262 | 1260 \leftrightarrow 1250 | 1250 | 1265 |
| 1170 BH δ | 1185 | 1130-1120 | 1230 |
| 1125 BH δ | 1130 BH δ | 1100 BH δ | 1115 |
| | 1095 | 1065-1040 | |
| 1000 NR ν | 1005 NR ν | 975 NR ν | 960 NR ν |
| 855 NR ν | 985 NR ν | | |
| | 950 | | |
| 690 \leftrightarrow 670 BN ν | 845 NR ν | 835 NR ν | 830 NR ν |
| | 690 BN ν | 715-695 BN ν | 700 \leftrightarrow 800 BN ν |
| | 640 BX ν | BX ν | BX ν |
| 440 NR δ | 470 BX ν | 500 BX ν | 530 BX ν |
| 345 NR δ | 420 NR ν | 440 NR δ | 440 NR δ |
| | 330 | 345 | 375 |
| | 310 | 315 | 330 |

It was this region which allowed rapid positive identification of the chloro-substituted adducts.

The spectrum of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ (Figure 22) was characterized mainly by the shift to higher wave numbers of the doublet BH stretching frequency, and the 300-600 cm^{-1} region.

The spectrum of $(\text{CH}_3)_3\text{NBHCl}_2$ (Figure 23) was characterized mainly by the singlet BH stretching frequency at 2480 cm^{-1} , two peaks at 1065 and 1040 cm^{-1} and the 300-600 cm^{-1} region. In identifying a mixture of $(\text{CH}_3)_3\text{NBH}_3$ and $(\text{CH}_3)_3\text{NBHCl}_2$, the doublet BH stretch of the $(\text{CH}_3)_3\text{NBH}_3$ and the two peaks at 1065-1040 for $(\text{CH}_3)_3\text{NBHCl}_2$ were the most prominent distinguishing features.

A comparison of the 300-600 cm^{-1} region in the infrared spectra of $(\text{CH}_3)_3\text{NBH}_3$, $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$, $(\text{CH}_3)_3\text{NBHCl}_2$ and $(\text{CH}_3)_3\text{NBCl}_3$ is shown in Figure 24.

Tentative assignments were made based on Taylor's assignments for $(\text{CH}_3)_3\text{NBH}_3$ and $(\text{CH}_3)_3\text{NBCl}_3$ (41), noting that the peaks shift to higher wave numbers as chlorines are substituted onto the boron.

Nuclear magnetic resonance spectra

The B^{11} nuclear magnetic resonance spectra of trimethylamine borane, trimethylamine monochloroborane, trimethylamine dichloroborane, trimethylamine trichloroborane, trimethylamine tribromoborane, and trimethylamine

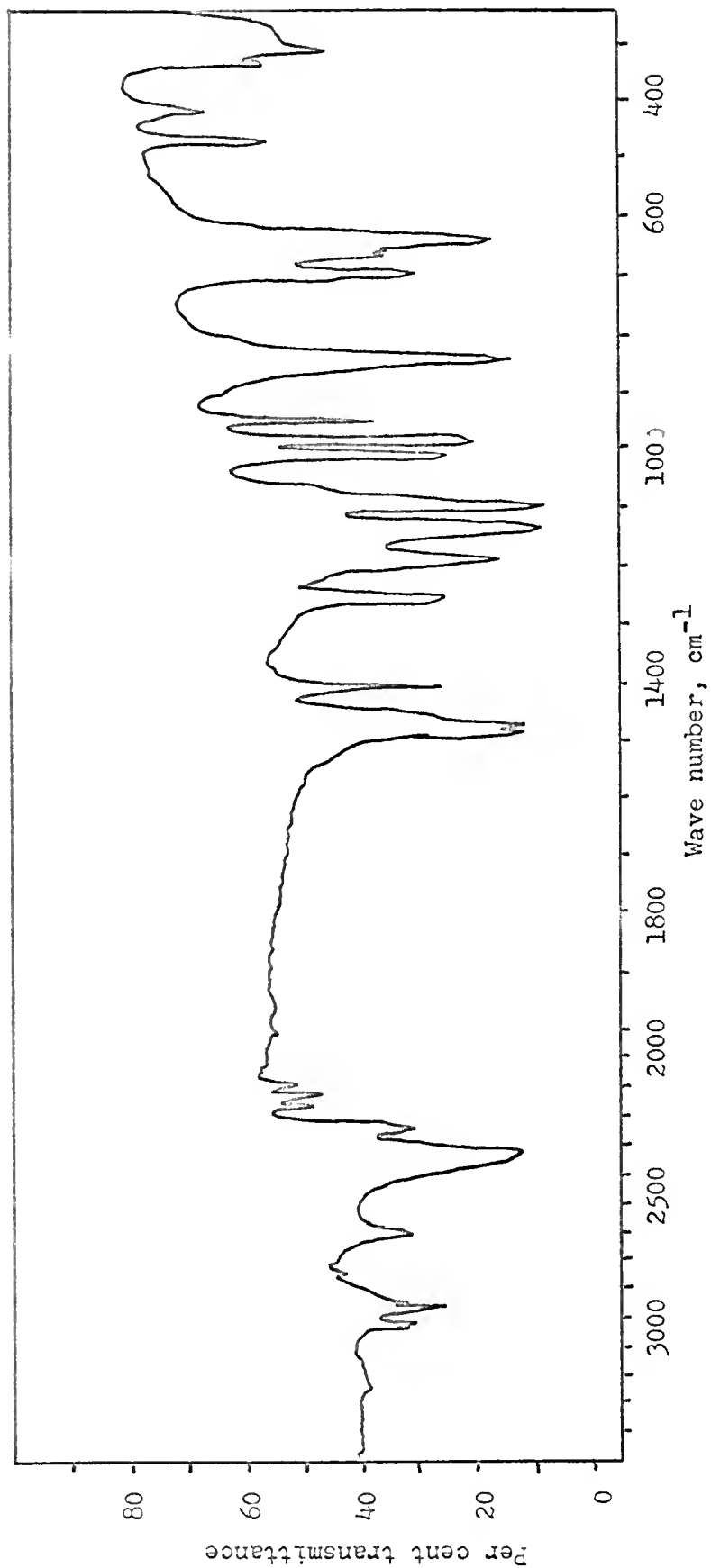


Fig. 22.---Infrared spectrum of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$.

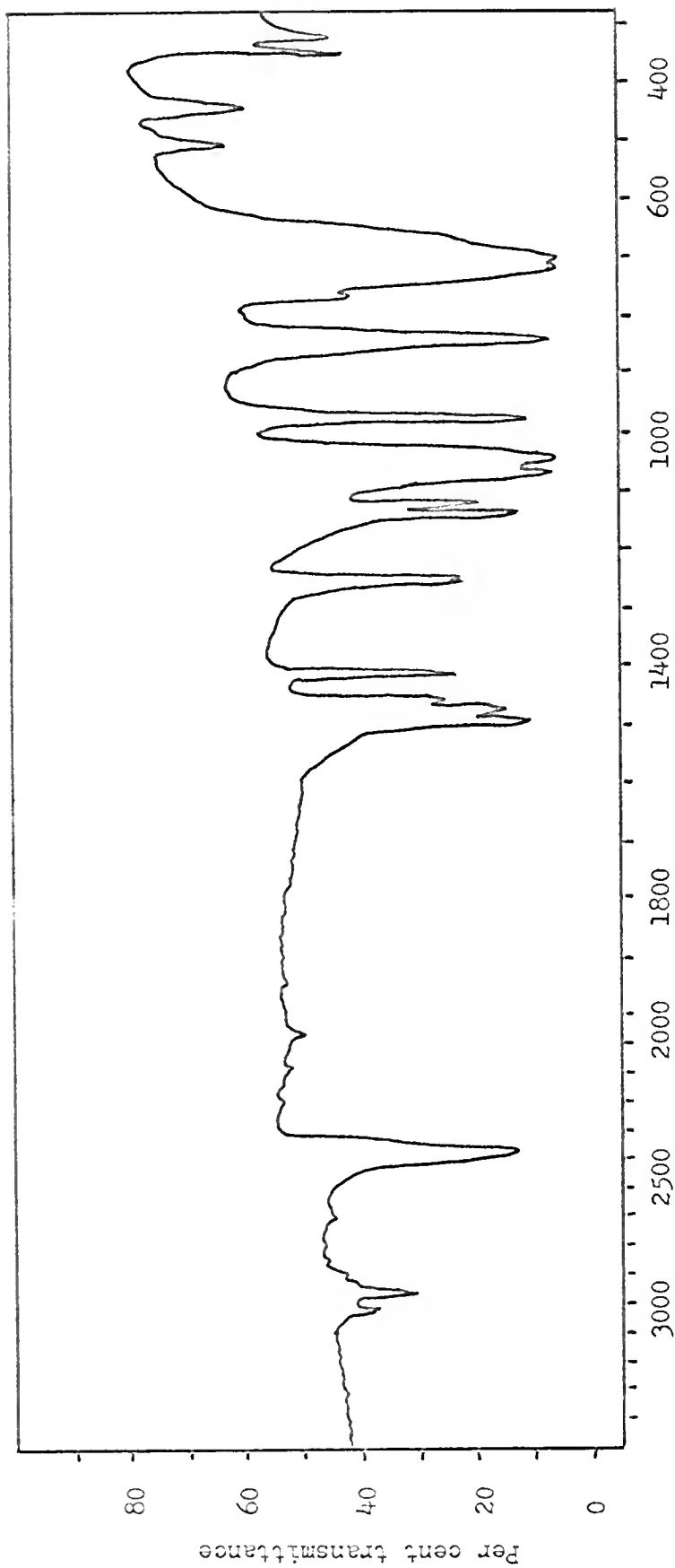


Fig. 23.--Infrared spectrum of $(\text{CH}_3)_3\text{NBHCl}_2$.

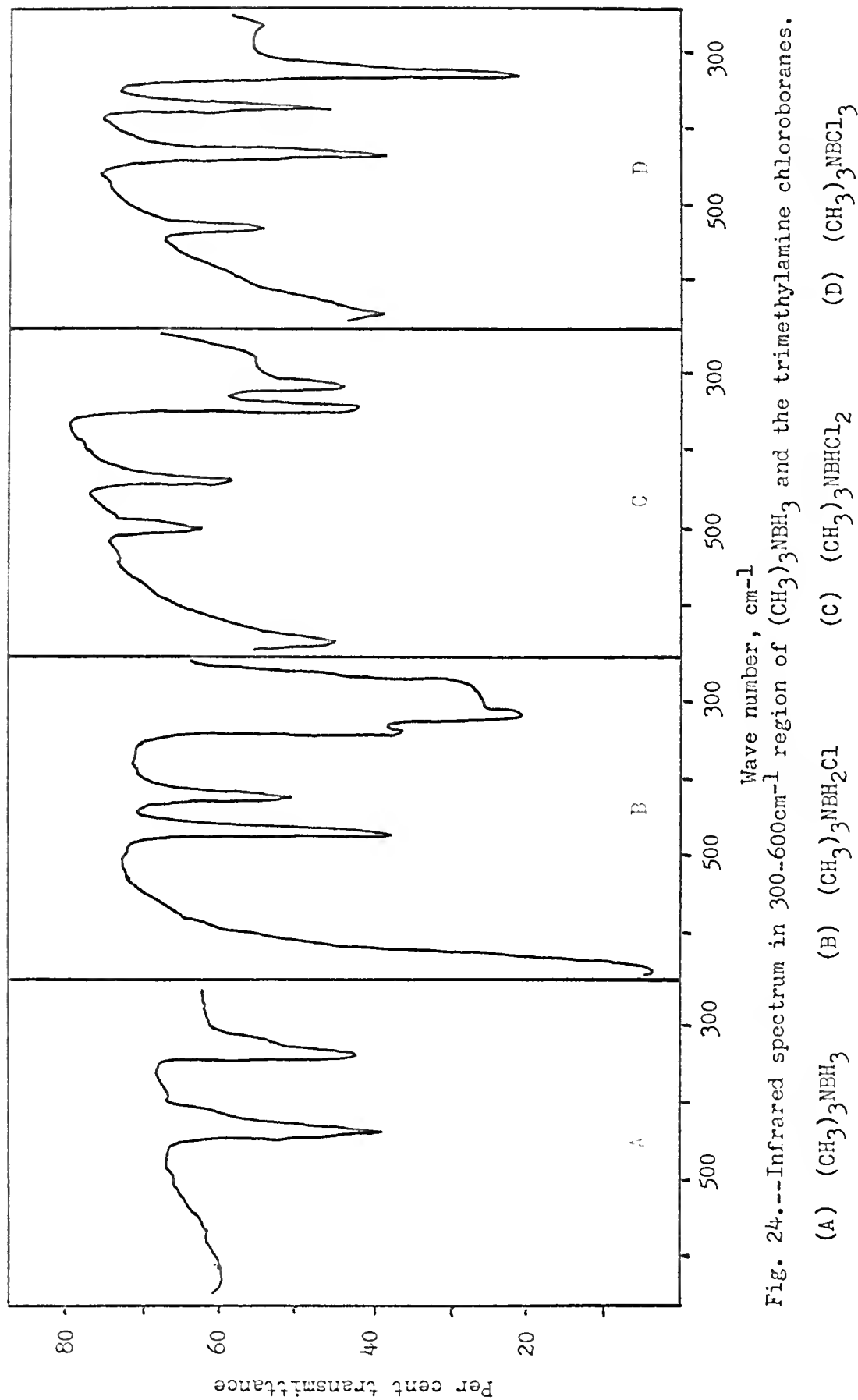


Fig. 24.---Infrared spectrum in $300\text{--}600\text{cm}^{-1}$ region of $(\text{CH}_3)_3\text{NBH}_3$ and the trimethylamine chloroboranes.

trifluoroborane were obtained at 19.3 megacycles, using a Varian DP 60 spectrometer. The results are given in Table 16.

The B^{11} NMR spectra were obtained to determine if on chloro substitution the electronic density about the boron atom decreased. This was predicted by the inductive effect which was used to explain the change in reactivity of the BH bond. The results confirmed the arguments. The measured chemical shift of $(CH_3)_3NBH$ of +26.1 referred to $B(OCH_3)_3$ agreed with that reported by Phillips, Miller, and Muetterties (33) of +24.9.

The spectra of the monochloro and dichloro adducts showed splitting due to coupling between the boron and hydrogen atoms. The monochloro adduct showed the boron peak split into three peaks ($2I + 1$) and the dichloro adduct showed the boron peak split into two peaks. These spectra may be seen in Figure 25 and 26.

The trend in the chemical shift of $(CH_3)_3NBr_3 > (CH_3)_3NBF_3 > (CH_3)_3NCl_3$ agreed with the trend found for the triethylamine, pyridine, and $(C_6H_5)_2CO$ adducts of the trihaloboranes by Gates, McLaughlan and Mooney (14).

The chemical shift for $(CH_3)_3NBF_3$ was greater than that for $(CH_3)_3NCl_3$ which implied a greater electronic density on the boron atom for the trifluoro adduct than the

TABLE 16

 B^{11} NUCLEAR MAGNETIC RESONANCE SPECTRAL RESULTS

| Compound | Solvent | ppm Referred to $B(OCH_3)_3$ | BH Coupling Con- stant Cycles per Second |
|-------------------|----------|---------------------------------|--|
| $(CH_3)_3NBH_3$ | C_6H_6 | +26.1 | 98 |
| $(CH_3)_3NBH_2Cl$ | C_6H_6 | +20.3 | 136 |
| $(CH_3)_3NBHCl_2$ | C_6H_6 | +13.3 | 148 |
| $(CH_3)_3NBCl_3$ | $CHCl_3$ | +10.4 ^a | |
| $(CH_3)_3NBF_3$ | $CHCl_3$ | +18.0 ^a | |
| $(CH_3)_3NBBBr_3$ | $CHCl_3$ | +22.3 ^a | |

^aCompound not soluble enough to get recorded spectra.
Chemical shift data taken from oscilloscope.

$(CH_3)_3NBH_2Cl$ CH_2Cl_2 +8.3 MAY 7, 1969 B.M.

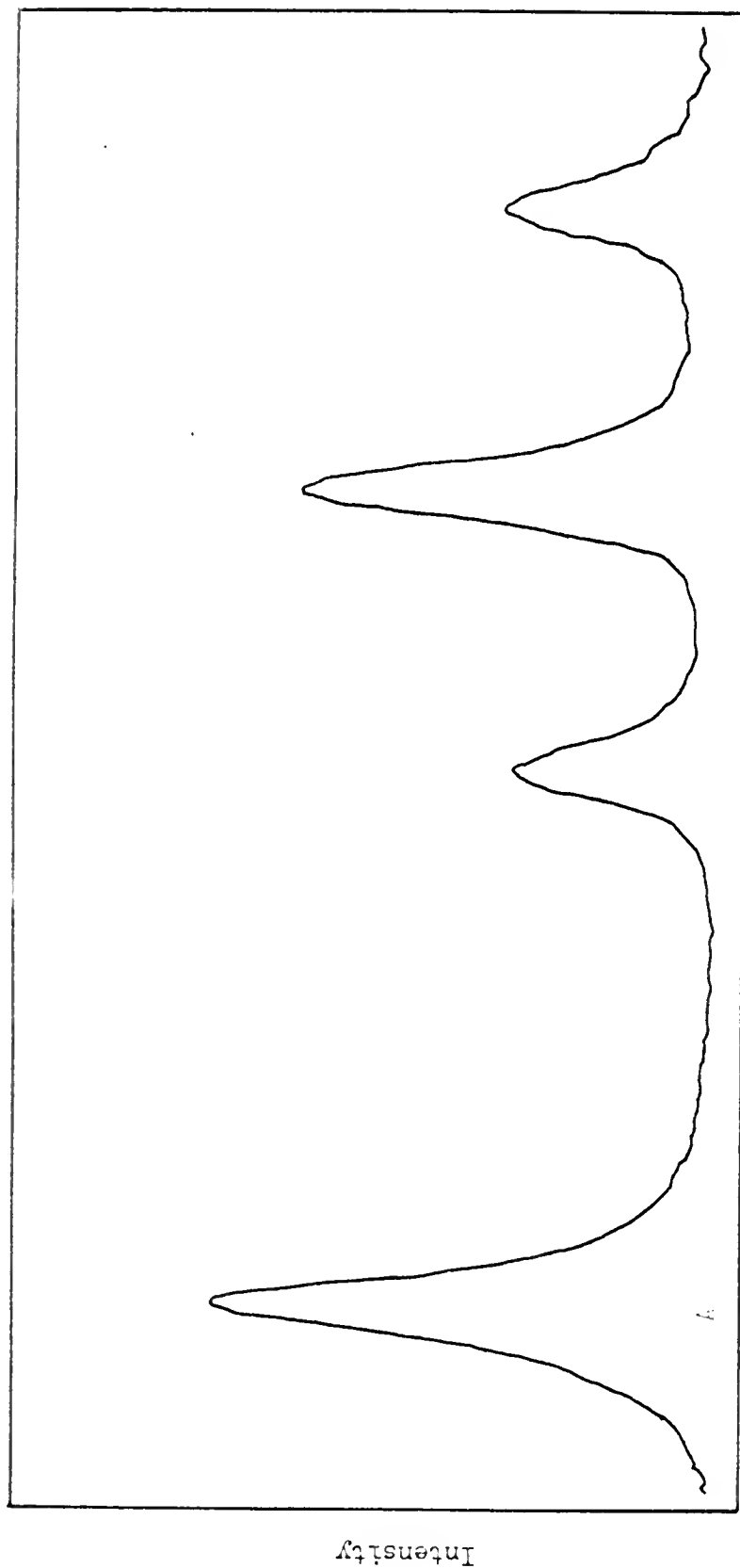


Fig. 25.---B11 Nuclear magnetic resonance spectrum of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ relative to $\text{B}(\text{OCH}_3)_3$.

(A) $\text{B}(\text{OCH}_3)_3$ reference peak.

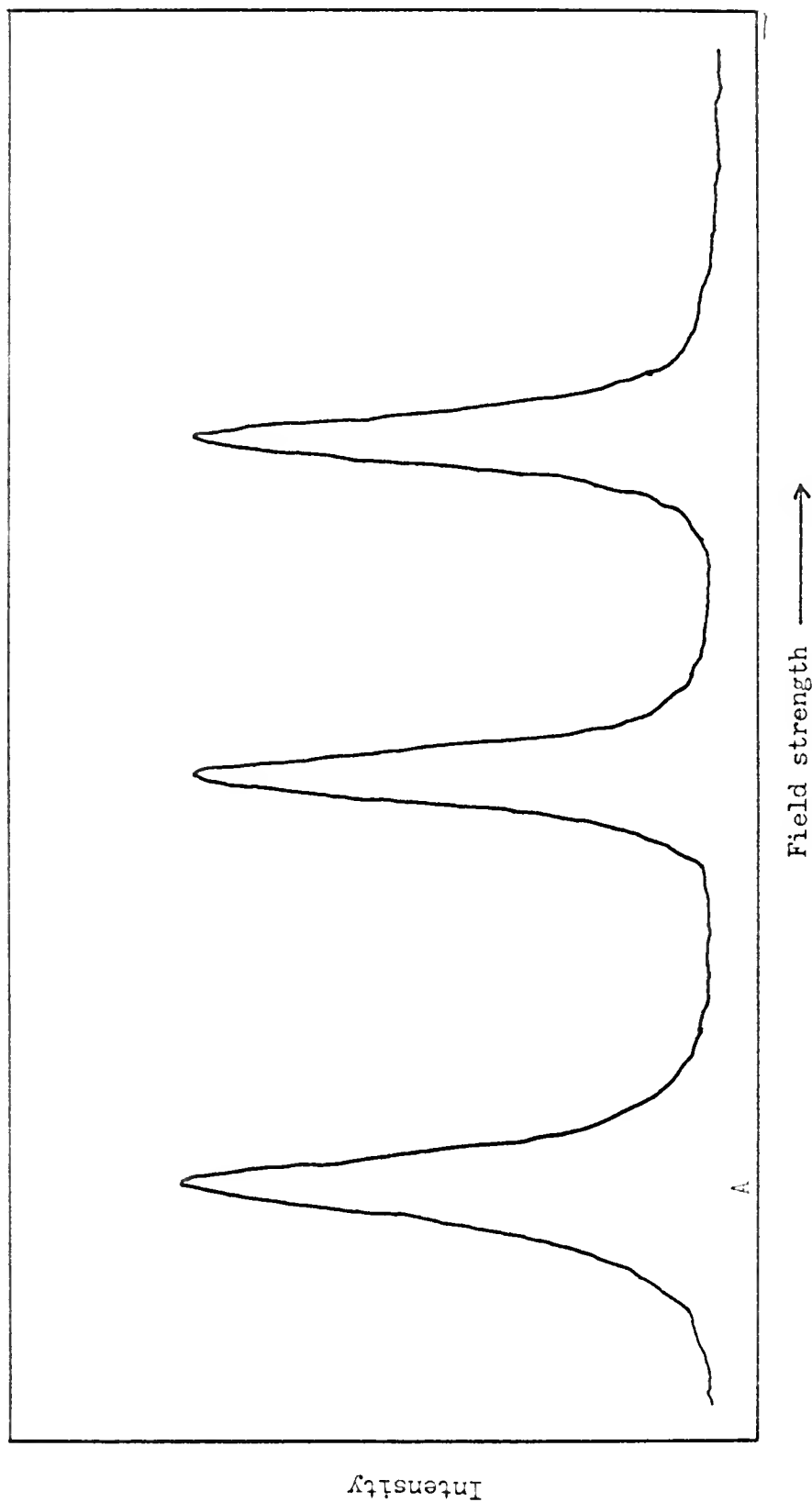


Fig. 26.---B¹¹ Nuclear magnetic resonance spectrum of $(\text{CH}_3)_3\text{NBHCl}_2$ relative to $\text{B}(\text{OCH}_3)_3$.

(A) $\text{B}(\text{OCH}_3)_3$ reference peak.

trichloro adduct. This was contrary to what would be expected from the consideration of electronegativities. However, the trend in the chemical shifts may be explained by a back donation of the fluorines' electron density onto the boron atom by a $p^\pi-p^\pi$ type system. This effect has been found to occur in other boron-fluorine compounds, and used to explain the behavior of the compounds.

Reaction of $(CH_3)_3NBH_3$ and $HgCl_2$

General procedure for reaction in ether.--Trimethylamine borane (13.7 mmoles) was dissolved in 200 ml of ether and stirred magnetically. Mercuric chloride (64.8 mmoles) was added to the ether solution and the stirring continued for the desired time.

The amounts of reactants were those found convenient to use. A reaction temperature of 0° to $36^\circ C$ did not change the products which were produced. A reaction time of thirty minutes to several hours did not appear to control which products were recovered. This reaction procedure did not give complete reaction considering the reaction stoichiometry. In all cases a mixture of amine chloroboranes was recovered, and the $HgCl_2$ did not react completely to give Hg_2Cl_2 which was identified by an x-ray diffraction pattern. Even large excesses of $HgCl_2$ would not drive the reaction to completion.

Slow addition of the HgCl_2 via a Soxhlet extractor was found to give a complete reaction to $(\text{CH}_3)_3\text{NBHCl}_2$ whenever four moles of HgCl_2 per one mole $(\text{CH}_3)_3\text{NBH}_3$ were used. When two moles HgCl_2 per one mole $(\text{CH}_3)_3\text{NBH}_3$ were used, in attempting to prepare $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$, the recovered product contained a small amount of $(\text{CH}_3)_3\text{NBHCl}_2$ in addition to the desired product.

The method for the extraction of boron-containing compounds from this reaction system was the same as that described in the reaction of $(\text{CH}_3)_3\text{NBH}_3$ and HgCl_2 at ether reflux. Benzene could be used as an extracting solvent, but an ether extraction followed by a hot CCl_4 extraction was found to be sufficient, provided excess solvent was used in each case.

The results of these reactions were listed in Table 17.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and HgCl_2 on a large scale

Trimethylamine borane (0.137 mole) was placed in a two liter, three-necked round bottom flask containing one liter of diethyl ether. One neck of the flask contained a Soxhlet extractor with a filter thimble containing mercuric chloride (0.553 moles), the center neck of the flask contained a Teflon wing-stirrer, and the last neck contained a glass plug.

TABLE 17
REACTIONS OF $(\text{CH}_3)_3\text{NBH}_3$ AND HgCl_2

| Mmoles $(\text{CH}_3)_3\text{NBH}_3$ | HgCl_2 | Temperature | Time | Final Products ^a |
|---|-----------------|--------------|--|--|
| 14.1 | 28.2 | 0° | 1/2 hr. | $(\text{CH}_3)_3\text{NBH}_3$ $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ $(\text{CH}_3)_3\text{NBHCl}_2$ |
| 13.9 | 27.9 | 0° | 1 hr. | $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ $(\text{CH}_3)_3\text{NBHCl}_2$ |
| 15.1 | 30.4 | ether reflux | 16-1/2 hrs. room temp. overnight | $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ $(\text{CH}_3)_3\text{NBHCl}_2$ ^b |
| 14.0 | 56.1 | ether reflux | 20 1/2 hrs. room temp. overnight | $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ $(\text{CH}_3)_3\text{NBHCl}_2$ |
| 137 | 265 | 0° | 1 1/2 hrs. | $(\text{CH}_3)_3\text{NBH}_3$ $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ |
| 138 | 552 | 0° | 1 hr. 10 5/6 hrs. | $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ $(\text{CH}_3)_3\text{NBHCl}_2$ |

Table 17 (cont'd)

| Mmoles (CH ₃) ₃ NBH ₃ | HgCl ₂ | Temperature | Time | Final Products ^a |
|--|-------------------|----------------------------|-----------------------|--|
| 137 | 553 | ether reflux room temp. | 50 hrs. 45 hrs. | (CH ₃) ₃ NBHCl ₂ |
| 63.2 | 480 | 150° autoclave | 3 hrs., 35 minutes | (CH ₃) ₃ NBHCl ₂ (CH ₃) ₃ NBCl ₃ |
| 30.8 | 61.6 | 35-100° autoclave | 9 hrs. | (CH ₃) ₃ NBH ₂ Cl (CH ₃) ₃ NBHCl ₂ (CH ₃) ₃ NBCl ₃ |
| (CH ₃) ₃ NBH ₂ Cl | | | | |
| 3.60 | 11.4 | 0° room temp. | 1 hr. 1 yr. | (CH ₃) ₃ NBHCl ₂ |
| (CH ₃) ₃ BHCl ₂ | 5.59 | 0° room temp. | 1 hr. 24 hrs. | (CH ₃) ₃ NBHCl ₂ |
| 2.75 | 5.59 | | | |

^aBy infrared analysis.^bSmall amount present.

As the ether refluxed through the Soxhlet, it dissolved the HgCl_2 . This gave a relatively slow addition of HgCl_2 to the $(\text{CH}_3)_3\text{NBH}_3$ solution.

The reaction was followed by infrared analysis of the reaction mixture. Aliquots of the ether solution were removed, the solvent removed from the aliquot portion, and an infrared spectrum taken of the solid residue. The infrared spectrum after the reaction had refluxed for eighteen hours and held at room temperature for twelve hours was that of pure $(\text{CH}_3)_3\text{NBHCl}_2$. The reaction was continued for ninety-five hours, but no change was observed in the infrared spectra.

The BN compounds were extracted from the reaction mixture as described previously. The procedure gave a white product, recrystallized from CCl_4 , in 80.3 per cent yield.

A commercial analysis gave:

| Per Cent | C | H | N | Cl | B |
|---|-------|------|------|-------|------|
| Found | 24.68 | 6.89 | 9.59 | 47.77 | 7.93 |
| Calculated for $(\text{CH}_3)_3\text{NBHCl}_2$ | 25.41 | 7.11 | 9.88 | 50.00 | 7.62 |

This material softened at 146° and was a liquid at 154° . In a sealed tube it melted at 144 to 149°C .

The infrared spectrum agreed with the spectra obtained for $(\text{CH}_3)_3\text{NBHCl}_2$ when prepared by other methods. The spectra showed a singlet BH stretching frequency at 2480 cm^{-1} , two intense peaks at 1065 and 1040 cm^{-1} , and less intense peaks at 500 , 440 , 345 , and 315 cm^{-1} as the distinguishing peaks.

Reaction of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and HgCl_2

Trimethylamine monochloroborane (3.6 mmoles) was placed in a two-neck round bottom flask. Mercuric chloride (11.4 mmoles) was placed in a tipping tube connected to the reaction flask in one neck; in the other neck of the flask, there was a stopcock adapter for connection to the vacuum system. The reaction flask was cooled to 0° and evacuated. Ether (75 ml) was distilled from CaH_2 into the reaction flask at liquid nitrogen temperature; the reaction flask was warmed to 0° and stirred magnetically. The HgCl_2 was tipped into the ether solution. After two hours at 0° , the reaction was cooled to liquid nitrogen temperature and less than 0.5 mm pressure was measured in the vacuum system. The reaction system was then warmed to room temperature for eighteen hours, and again the reaction was cooled but no non-condensable gas pressure was measured.

Commercial "anhydrous" ether was distilled into the reaction system to determine if trace amounts of water might

cause a reaction. The reaction system was then warmed to 0° for two hours, and then to room temperature for fourteen hours with no visible changes occurring. The solvent and other volatile reaction products were transferred from the reaction flask, and the reaction flask containing the solid reaction residue was then set aside at room temperature with the stopcock closed.

After thirteen months and twenty-one days, the solid reaction residue was heated with CCl_4 . The hot CCl_4 solution was filtered. The filtrate was reacted with mercury metal, heated and again filtered hot. A product was precipitated on cooling the CCl_4 solution. This product gave 26.7 per cent pure yield of $(\text{CH}_3)_3\text{NBHCl}_2$. This product melted at 150-154°. Its infrared spectrum agreed with that of $(\text{CH}_3)_3\text{NBHCl}_2$. There was no spectral evidence for $(\text{CH}_3)_3\text{NBCl}_3$ in this product.

Attempted reaction of $(\text{CH}_3)_3\text{NBHCl}_2$ with HgCl_2

Trimethylamine dichloroborane (2.75 mmoles) was dissolved in 100 ml of diethyl ether, and cooled in an ice bath to 0°. Mercuric chloride (5.59 mmoles) was added to the solution and the reaction mixture stirred magnetically using a Teflon coated stirring bar. The reaction flask was closed to the atmosphere by a glass stopper. After one hour at 0°, the HgCl_2 had dissolved and the reaction system was

homogeneous. The reaction mixture was then warmed to room temperature.

After the mixture stood for twenty-four hours, mercury metal was added to convert the Hg(II) to Hg(I). The mixture was filtered and the residue washed with excess ether. The ether was evaporated from the filtrate and a solid product remained.

The recovered product melted at 146-148°, and had an infrared spectrum identical to that of $(\text{CH}_3)_3\text{NBHCl}_2$. No spectral evidence for $(\text{CH}_3)_3\text{NBCl}_3$ was observed. The starting amine borane was recovered in 93 per cent yield.

The same two reactants were mixed in a ratio of one mole of $(\text{CH}_3)_3\text{NBHCl}_2$ to two moles of HgCl_2 , then slurried in ether. The ether was evaporated and the solid material remained at room temperature for twenty-six days. The $(\text{CH}_3)_3\text{NBHCl}_2$ was recovered by the previous procedure in 85.4 per cent yield. The infrared spectrum agreed with that of the starting material. No spectral evidence of $(\text{CH}_3)_3\text{NBCl}_3$ was observed in the recovered material.

Relative rates of reaction of $(\text{CH}_3)_3\text{NBH}_3$ with HgCl_2 and HCl in ether at 0°

Trimethylamine borane (1.59 mmoles) was sublimed into a tube which could later be turned so the solution would flow into the reaction flask, and could be closed

from the reaction flask by a stopcock. The trimethylamine borane was dissolved in 15 ml of anhydrous ether. The tipping tube was connected to a three-neck 300 ml round bottom flask, whose center neck had a stopcock adapter for connection to the vacuum system and the other neck was plugged. Mercuric chloride (3.20 mmoles) was placed in the reaction flask and 50 ml of anhydrous ether added. The entire reaction set-up was condensed and evacuated, and the solutions degassed by warming to room temperature, condensing and evacuating the set-up. Hydrogen chloride gas was condensed into the vacuum system and a measured amount (1.60 mmoles) was condensed into the reaction flask.

The reaction flask was warmed to room temperature and stirred magnetically. The HgCl_2 would not dissolve completely. There was a slight residue of finely powdered HgCl_2 suspended in the ether.

The reaction flask was then cooled to 0° in an ice bath and the stirring continued. The tube containing the $(\text{CH}_3)_3\text{NBH}_3$ was washed into the reaction flask by condensing the ether vapor in the tube with dry ice and letting this liquid flow back into the reaction flask. By using this procedure all the $(\text{CH}_3)_3\text{NBH}_3$ was transferred into the reaction flask within a few minutes.

The reaction flask was stirred at 0° for one hour. The products were then condensed and the non-condensable

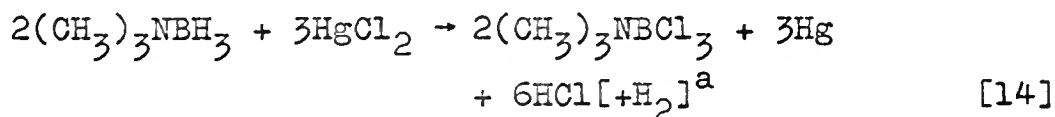
gas was transferred, using a Toepler pump, into a calibrated bulb. The amount of non-condensable gas was 0.36 mmoles.

This implied that only 0.36 mmoles of the 1.59 (20 per cent) of $(\text{CH}_3)_3\text{NBH}_3$ reacted with the HCl gas. In other experiments on this scale and under these conditions HgCl_2 was found to react with $(\text{CH}_3)_3\text{NBH}_3$ to give $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and some $(\text{CH}_3)_3\text{NBHCl}_2$. It was concluded that in the reaction time the $(\text{CH}_3)_3\text{NBH}_3$ would be completely reacted and that the reaction with the HgCl_2 was faster than the reaction with HCl by at least a factor of four.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and HgCl_2 in the autoclave

General procedure.--Trimethylamine borane and mercuric chloride were placed in the stainless steel autoclave which was immediately sealed. After a set period of time at the desired temperature, the gaseous products were released through a liquid N_2 trap, a mercury bubbler and collected in a water-filled inverted graduated cylinder. In this manner, the amount of non-condensable gas was determined. The solid materials were removed from the autoclave and extracted with hot carbon tetrachloride. The compounds extracted in the hot carbon tetrachloride were analyzed by obtaining infrared spectra. The results of the experiments are given in Table 17.

In each reaction, there was unreacted HgCl_2 and mercury metal present in the reaction mixture. Qualitative tests for other reaction products showed that the non-condensable product contained no infrared active material; a strong odor of HCl(g) was noticed in the workup of the compounds. Thus, the following equation may be written:



It may now be concluded that HgCl_2 will react with $(\text{CH}_3)_3\text{NBH}_3$ at 100° to produce the completely chlorinated trimethylamine borane adduct, and that the Hg(II) was reduced to Hg(0) .

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and HgCl_2 in presence of acetic acid in benzene

Trimethylamine borane (14.0 mmoles) was dissolved in 100 ml benzene (dried over "dri-Na") and 0.8 ml of glacial acetic acid (14.0 mmoles) pipetted into the solution. A slurry of HgCl_2 (28.2 mmoles) in benzene was added to the amine borane acetic acid solution. Judging from the appearance of the white precipitate, the reaction was slower than in ether or water solvents. After two hours and ten minutes at room temperature, the reaction mixture was filtered through excess anhydrous K_2CO_3 and the benzene removed from the filtrate using a rotating evaporator. The

^aThe hydrogen was produced by the reaction of HCl and $(\text{CH}_3)_3\text{NBH}_3$.

infrared spectrum of the material recovered from the benzene showed that the compound was primarily $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ with a small amount of $(\text{CH}_3)_3\text{NBHCl}_2$. Considering the product to be pure $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$, the yield was 82 per cent.

The reaction was repeated using a larger molar ratio of acetic acid to amine borane. Trimethylamine borane (14.1 mmoles) and 8 ml of glacial acetic acid (140.0 mmoles) were dissolved in benzene and solid HgCl_2 (28.6 mmoles) was added. After two hours and ten minutes at room temperature a product was recovered from the benzene using the procedure in the previous experiment. The infrared spectrum of the material showed it to be mainly $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ with a small amount of $(\text{CH}_3)_3\text{NBHCl}_2$. The material was recovered in 73.0 per cent yield of pure $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$. Thus, the acetic acid did not appear to affect the reaction under these conditions.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and HgCl_2 in water and in potassium chloride solutions

General procedure.--Trimethylamine borane dissolved in water (or KCl solution) was added to a water (or KCl) solution of mercuric chloride and the solution stirred magnetically for the desired period of time. A product was then extracted by adding an equal volume of benzene to the reaction solution and the mixture shaken vigorously. The water-benzene phases were separated using a separatory

funnel, and the benzene layer dried over anhydrous potassium carbonate. After removal of the benzene in a rotating evaporator, an infrared spectrum was taken of the residue.

The results of the experiments are given in Table 18.

Attempts to isolate other BN containing products were not successful. No other BN compounds were evidently produced during the reaction in water. The yield of monochloro adduct would imply that it was produced in a side reaction. An x-ray diffraction pattern of the water-insoluble residue from the reaction was similar to that of mercurous chloride, the only difference being a broad peak at 26° which was not present in the pattern of Hg_2Cl_2 . The change in pH with time for these reactions was examined.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and HgCl_2 in water--the change in pH with time

The pH was followed by a Model SR Sargent Recorder equipped with a resistance-matching adapter (S-72172 Sargent pH adapter) for measurement with Beckman glass and calomel electrodes. The apparatus was calibrated using standard buffer solutions to have a pH range of 0 to 12.5 over a one millivolt range. The electrodes were placed in a mercuric chloride solution, the chart speed set at one inch per minute, and then a trimethylamine borane solution was added to the cell. A white precipitate formed and the pH dropped immediately.

TABLE 18

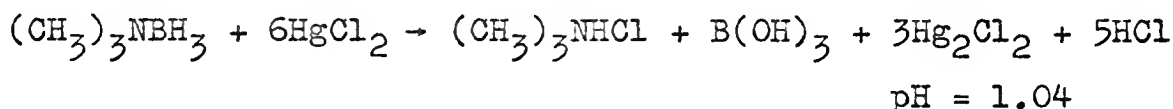
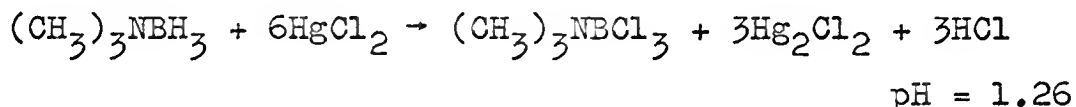
REACTION OF $(\text{CH}_3)_3\text{NBH}_3$ AND HgCl_2 IN WATER AND KCl SOLUTIONS

| $(\text{CH}_3)_3\text{NBH}_3$ mmoles | HgCl_2 mmoles | Solvent | Reaction Time | $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ Per Cent Yield |
|---|---------------------------|----------------------|--------------------|--|
| 13.8 | 55.1 | H_2O | 5 min. | 8.6 |
| 7.06 | 42.4 | 1M KCl | 5 min. | 2 |
| 6.92 | 41.6 | Sat'd. KCl | 10 min. (23.5°) | 1.3 |
| 7.02 | 42.2 | 1M KCl | 30 min. | 1.4 |
| 6.97 | 14.0 | 1M KCl | 5 min. | 0.7 |

In the reaction of $(\text{CH}_3)_3\text{NBH}_3$ (5.02 mmoles) and HgCl_2 (30.1 mmoles), the pH changed from 3.15 in the HgCl_2 solution to 1.10 within six seconds after the addition of the amine borane solution. After twenty-five seconds the pH was 1.05 and did not change further in thirty minutes.

Considering the two possible reactions which could produce a strong acid in the solution and calculating the pH of the solution for complete reaction, the resulting pH, in a volume of 275 ml, of the experiment (1.05) agreed more closely with the reaction to produce boric acid (1.04).

The possible reactions are:



Another reaction was carried out using the same procedure but a different stoichiometry. Trimethylamine borane (0.518 mmoles) and mercuric chloride (3.00 mmoles) were reacted and the resulting solution was titrated with 0.1M NaOH solution. In this reaction, the pH changed from 4.90 in the HgCl_2 solution to 2.65 within six seconds after the addition of the amineborane. After two minutes the pH was 1.75 and remained constant for five minutes. (See Figure 27.) The solution was then titrated to a pH of 9.0 with 0.1M NaOH solution and the pH remained constant for 13 minutes.

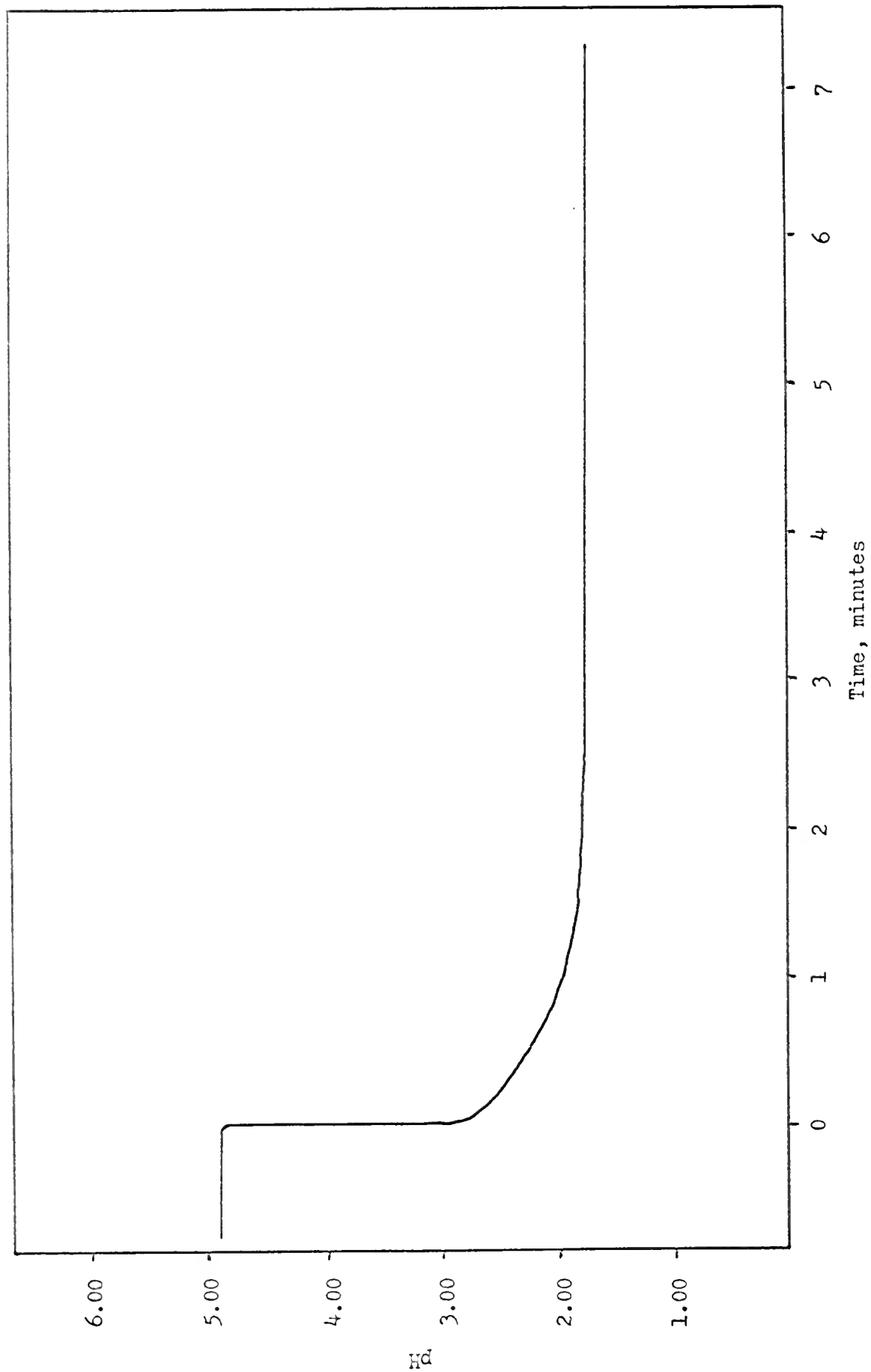


Fig. 27.---Change in pH with time during the reaction of $(\text{CH}_3)_3\text{NBH}_3$ and HgCl_2 in water.

The end point of the titration at pH of 5.0^a showed that 2.34 mmoles of H_3O^+ had been produced by the reaction. If the amine borane-mercuric chloride reaction had given $(\text{CH}_3)_3\text{NBHCl}_2$ then 1.55 mmoles of H_3O^+ would have been present in the solution; if the reaction had gone to boric acid then 2.59 mmoles of H_3O^+ would have been expected. Again, the data implied that the end result of the amine borane-mercuric chloride reaction in water was boric acid and that any trimethylamine monochloroborane recovered from the reaction must have been produced in a side reaction. This point was considered further in the discussion of the experimental results.

Reaction of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and $(\text{CH}_3)_3\text{NBHCl}_2$ with HgCl_2 in water--the change in pH with time

The apparatus to measure the pH was the same as that used in the trimethylamine borane experiments. Trimethylamine monochloroborane (1.57 mmoles) was dissolved in 100 ml water using ethanol (2 ml) to wet the amine borane, and the electrodes were placed in the solution. The pH of the solution decreased slightly before the addition of mercuric chloride-water solution. On addition of the mercuric chloride, a dark precipitate formed but it turned white within a few minutes. The rate of change in pH was much

^aAt this end point only the strong acid was titrated.

slower than in the trimethylamine borane reaction as may be seen in Figure 28.

The same procedure was followed in the reaction between trimethylamine dichloroborane (2.54 mmoles) and mercuric chloride (5.17 mmoles). Trimethylamine dichloroborane would not dissolve in 100 ml water or in a 20:1 water-ethanol mixture. The electrodes were placed in the trimethylamine dichloroborane-water-ethanol slurry and the pH decreased steadily. The addition of the mercuric chloride solution did not affect the rate of change of pH in the solution, but the pH continued to decrease steadily (see Figure 28). No visual evidence of a Hg_2Cl_2 precipitate was noted in this reaction as had been in the previous reactions. The data implied that the amine dichloroborane was reacting with the water and that mercuric chloride did not significantly affect this reaction.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and excess $\text{HCl}(\text{g})$

Trimethylamine borane (13.8 mmoles) was placed in a glass lined autoclave. The autoclave was closed, attached to a vacuum system, immersed in liquid nitrogen and evacuated. Hydrogen chloride was condensed into the vacuum system and a measured amount (37.1 mmoles) transferred into the autoclave. The autoclave was warmed to room temperature and then heated at $100 \pm 5^\circ$ for twenty-four hours.

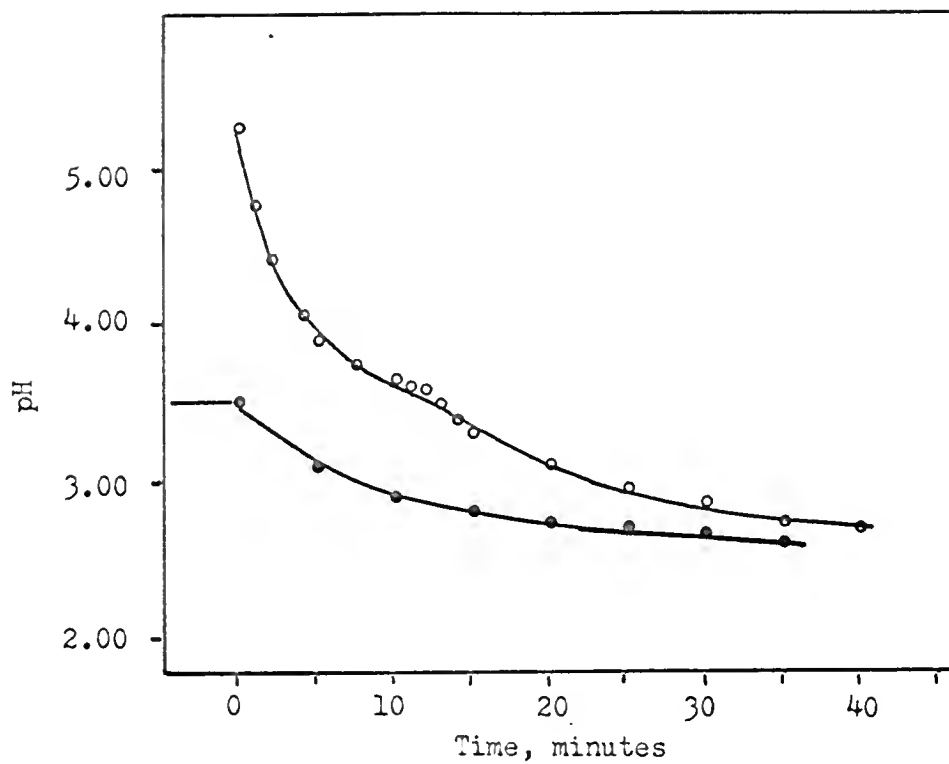


Fig. 28.--Change in pH with time during the reaction of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and $(\text{CH}_3)_3\text{NBHCl}_2$ with HgCl_2 in water.

(●) $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and (○) $(\text{CH}_3)_3\text{NBHCl}_2$.

The autoclave, at room temperature, was opened and the volatile portion was allowed to pass through a liquid N_2 trap, a mercury bubbler, and into a water-filled inverted graduated cylinder. A non-condensable fraction (25.4 mmoles) was collected.

A solid product was removed from the glass liner. This material was sublimed from room temperature to -78° . It was then recrystallized from hot CCl_4 . The pure yield was on the order of 45 to 50 per cent $(CH_3)_3NBHCl_2$.

Analysis of the product showed two moles of chlorine per mole of boron.

| Per Cent | B | Cl ⁻ |
|----------|------|-----------------|
| Found | 7.92 | 48.4, 47.6 |
| Calcd. | 7.62 | 50.00 |

The melting point of this material was $147-148^\circ$.

The infrared spectrum, identical to that of $(CH_3)_3NBHCl_2$, showed a singlet BH stretching frequency at 2480 cm^{-1} , two intense peaks at 1065 and 1040 cm^{-1} , and less intense peaks at 500 , 440 , 345 , and 315 cm^{-1} as the distinguishing peaks.

Reaction of $(CH_3)_3NBH_3$ and $HCl(g)$ in benzene

Trimethylamine borane (149.0 mmoles) was dissolved in 300 ml of benzene, and a mixture of trimethylamine borane and the monochloro adduct (9.3236 g) was added to the solu-

tion. Hydrogen chloride was bubbled slowly through a mercury bubbler and into the amine borane-benzene solution at room temperature. After six hours, the benzene solution was yellowish in color and bubbling in the solution had ceased. The solution was then filtered and the solvent partially removed from the filtrate by distillation at atmospheric pressure until approximately 50 ml of benzene remained. This was removed using the rotating evaporator. The remaining solid material was slightly yellowish in color, had a mp of 84-85°, ^a and the infrared spectrum showed only $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ to be present.

The exact yield of the reaction could not be determined since the amount of amine borane was not known. The weight gained (5.944 g) by the solid material during the reaction indicated that the reaction must have been almost a quantitative one. This is a recommended method for the preparation of trimethylamine monochloroborane.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and concentrated $\text{HCl}(\text{aq})$ in water

A trimethylamine borane-saturated water solution (10 ml) was added to concentrated hydrochloric acid (2 ml) and shaken vigorously for five minutes. The solution was then neutralized by adding 5 ml of 6M NaOH solution. ^b A

^aLiterature value (32) is 85°.

^bThe water layer turned pink on the addition of phenolphthalein.

product was extracted into benzene by twice adding approximately 25 ml of benzene, shaking and then separating the benzene-water phases. The benzene phase was dried over anhydrous K_2CO_3 , filtered and the solvent removed. The infrared spectrum of the recovered material showed a mixture of $(CH_3)_3NBH_3$ and $(CH_3)_3NBH_2Cl$.

The reaction was repeated using 15 ml of saturated amine borane solution and 3 ml of concentrated $HCl(aq)$. After neutralization the solution was cooled to room temperature before extraction with benzene. The infrared spectrum of the recovered product showed $(CH_3)_3NBH_2Cl$ but it also contained peaks which were similar to those in a spectrum of boric acid.

Reaction of $(CH_3)_3NBH_3$ and concentrated $HCl(aq)$ in benzene

Trimethylamine borane (14.7 mmoles) was dissolved in 50 ml of benzene in a separatory funnel and 2 ml of concentrated hydrochloric acid were added to the solution. After shaking vigorously for ten minutes, the water layer was removed; and the benzene solution was set aside for one hour. An infrared spectrum on the material remaining after removal of the benzene showed the product to be a mixture of $(CH_3)_3NBH_3$ and $(CH_3)_3NBH_2Cl$.

The experiment was repeated on a larger scale but the results were the same as in the previous experiment.

The reaction product was recovered in a yield of 40 per cent if it had been pure $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and concentrated $\text{HCl}(\text{aq})$ in carbon tetrachloride

Trimethylamine borane (14.2 mmoles) was dissolved in 50 ml of carbon tetrachloride, 5 ml of concentrated hydrochloric acid were added, and after ten minutes, the water layer was removed. Since there had been no visual evidence for a reaction occurring in the CCl_4 layer, e.g., bubbling, the solution was set aside open to the atmosphere. After three weeks, it was noticed that the CCl_4 had evaporated and a crystalline material was in the reaction flask. The infrared spectrum of this material showed it to contain only $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$. Therefore, a reaction must have occurred in the CCl_4 phase.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$, $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and $(\text{CH}_3)_3\text{NBHCl}_2$ with $(\text{CH}_3)_3\text{NHCl}$

General procedure.--The amine borane and the amine hydrochloride were placed in a stainless steel autoclave and heated for a set period of time at the desired temperature. After the autoclave cooled to room temperature, the gaseous products were released. In some experiments, the water-insoluble gaseous products were measured but since in all but one reaction the product was a mixture of compounds

the volume of gas had little meaning. The trimethylamine produced in the reaction could not be removed completely because a small quantity of it tended to remain adsorbed in the reaction mixture.

A product was extracted from the solid reaction residue with boiling carbon tetrachloride, the solution filtered hot, and the carbon tetrachloride removed from the filtrate, using a rotating evaporator. Infrared spectra were obtained on the solid residues. The results of the experiments are given in Table 19.

Reaction number I in Table 19 produced pure $(\text{CH}_3)_3\text{NBHCl}_2$. The compound had a melting point of 145-146°. A commercial analysis of this compound gave the following:

| Per Cent | C | H | N | Cl | B |
|---|-------|------|------|-------|------|
| Found | 25.36 | 7.06 | 9.83 | 50.09 | 7.55 |
| Calcd. for $(\text{CH}_3)_3\text{NBHCl}_2$ | 25.41 | 7.11 | 9.88 | 50.00 | 7.62 |

The yield of product from this reaction was 40 per cent.

These reactions gave poor yields and in most cases the product contained a hygroscopic material, probably some of the unreacted amine hydrochloride.

Occasionally, the solid reaction mixture removed from the autoclave was blue-green in color. The colored material was water soluble and on addition of dimethylglyoxime a red

TABLE 19

REACTIONS OF $(\text{CH}_3)_3\text{NBH}_3$ AND TRIMETHYLAMINE CHLOROBORANES WITH $(\text{CH}_3)_3\text{NHCl}$

| $(\text{CH}_3)_3\text{NBH}_3$ | $(\text{CH}_3)_3\text{NHCl}$ mmoles | Reaction Time, Hrs. | Reaction Temperature | Final Products by IR Analysis |
|-------------------------------|--|-------------------------------------|-------------------------|--|
| I. 16.5 | 63.0 | 11.5 | 150° | |
| | | 7.2 | 175° | |
| | | 16.3 | 185° | |
| | | remove gaseous products and reheat | | |
| | | 11.0 | 150° | |
| | | 5.5 | 175° | |
| | | 5 | 185° | $(\text{CH}_3)_3\text{NBHCl}_2$ |
| II. 19.5 | 77.2 | 3.7 | 150° | $(\text{CH}_3)_3\text{NBHCl}_2$ |
| | | 14.5 | 175° | $(\text{CH}_3)_3\text{NBH}_2\text{Cl}^a$ |
| | | 4 | 185° | |
| III. 18.6 | 92.6 | 2.5 | 150° | $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ |
| | | 50 | 185° | $(\text{CH}_3)_3\text{NBHCl}_2$ |
| III. 19.6 | 82.0 | 50 | 185° | $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ |
| | | | | $(\text{CH}_3)_3\text{NBHCl}_2$ |
| IV. 18.5 | 74.6 | 24 | 185° | |
| | | release gaseous products and reheat | | |
| | | 26 | 185° | $(\text{CH}_3)_3\text{NBHCl}_2$ |

Table 19 (cont'd)

| $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ | $(\text{CH}_3)_3\text{NHCl}$ mmoles | Reaction Time, Hrs. | Reaction Temperature | Final Products by IR Analysis |
|--|--|---|-------------------------|--|
| V. 16.1 | 16.2 | 15.3 | 150° | $(\text{CH}_3)_3\text{NBHCl}_2$ |
| | | 49.5 | 175° | $(\text{CH}_3)_3\text{NBCl}_3$ |
| VI. 16.1 | 16.3 | 20 | 150° | |
| | | release gaseous products, add more amine hydro- chloride | | |
| | 33.0 | 16 | 150° | $(\text{CH}_3)_3\text{NBHCl}_2$ |
| | | 8 | 175° | $(\text{CH}_3)_3\text{NBCl}_3$ |
| VII. 7.10 | 22.8 | 24 | 185° | Impure, hydro- scopic material, did contain a BH compound |

^aOnly a small amount of the compound present.

precipitate formed. This implied that Ni(II) was present in the reaction mixture. The only way this could be accounted for was by some side reaction between a reactant or product and the walls of the stainless steel autoclave.

Reaction of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ with SbCl_5

Antimony pentachloride (1.56 mmoles) was pipetted into a 50 ml round bottom flask containing trimethylamine monochloroborane (1.03 mmoles) in a Dri-Lab controlled atmosphere box. An immediate violent evolution of gas occurred. The flask was fitted with a vacuum system adapter, attached to the system and evacuated. All volatile materials were transferred from the flask. A Nujol mull was prepared on the non-volatile reaction residue and the infrared spectrum obtained using NaCl plates. The spectra did not show any BH stretching vibrations in the 2300-2500 cm^{-1} region, but all the peaks in the spectra agreed with either the spectrum of Nujol or the spectra of $(\text{CH}_3)_3\text{NBHCl}_3$.

The reaction was rerun under better controlled conditions.

Antimony pentachloride (3.91 mmoles) was distilled in the vacuum system into a flask containing trimethylamine monochloroborane (2.10 mmoles) and the reaction flask was warmed to -78° . Since there was no change of the pressure in the system after several minutes, the flask was warmed

to 0°. An immediate increase in pressure was noticed when the flask was first warmed, but at 0° the pressure continued to increase slowly. On warming to room temperature, a faster increase in pressure occurred and after forty-five minutes the flask was immersed in a liquid N₂ bath; a small amount of non-condensable gas was noted. The condensable gaseous product was distilled from the reaction flask into a flask containing 40 ml of 0.1M NaOH solution and warmed to room temperature. A back titration of the excess base with 0.1M standard HCl solution indicated that the gas contained 2.83 meq of acid, but the reaction product also contained a material which reacted with the phenolphthalein indicator which made the end point of this titration somewhat in doubt.

The solid reaction product was washed with 60 ml of diethyl ether to remove any antimony chlorides. Hot ethanol was used to extract a product from the ether insoluble material. The ethanol extracted product contained (CH₃)₃NBCl₃ according to its infrared spectrum.

The ether from a portion of the wash solution was distilled in the vacuum system and a yellowish residue remained. The residue turned a dark grey-black slowly over a period of two days. The other portion of the ether wash solution remained visually unchanged in the same period of time. The dark residue was washed with ether and hot ethanol.

A subsequent qualitative test for antimony (III) (18) on the remaining grey powder after reaction with nitric acid proved to be positive.

The ether in the remaining wash solution was removed and the same color change was noted. After one week, two large crystals were noticed in the top of the flask. The sealed tube melting points of these crystals and of sublimed antimony trichloride were both 73-74°. The reported (9) melting point is 73.4°.

From the reaction of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and SbCl_5 it may be concluded that the reaction produced an acidic gas, $(\text{CH}_3)_3\text{NBCl}_3$, and a grey powdery material which did contain antimony (or antimony III) and that the reaction with SbCl_3 did not occur in ether solution but did occur slowly at room temperature when the ether was removed.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$, $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$, $(\text{CH}_3)_3\text{NBHCl}_2$ and $(\text{CH}_3)_3\text{NBCl}_3$ with SbCl_3

Exploratory reactions between the amine boranes and antimony trichloride were done in the Dri-Lab controlled atmosphere box. The following observations were noted. SbCl_3 and $(\text{CH}_3)_3\text{NBH}_3$: The solids turned black upon contact and after two days the flask was coated with a metallic mirror. SbCl_3 and $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$: The solids reacted immediately to give a black material and liquid phase from which

gas evolved. SbCl_3 and $(\text{CH}_3)_3\text{NBHCl}_2$: On first contact, the solids changed to a liquid phase which after several minutes began to have dark specks of material in it which increased with time. The infrared spectrum of the liquid phase in Nujol on NaCl plates showed only the starting material, $(\text{CH}_3)_3\text{NBHCl}_2$ and perhaps some $(\text{CH}_3)_3\text{NBCl}_3$. The relative intensity of the BH stretching peak at 2480 cm^{-1} to the rest of the spectrum was less than it would have been if the material had been pure $(\text{CH}_3)_3\text{NBHCl}_2$. SbCl_3 and $(\text{CH}_3)_3\text{NBCl}_3$: No evidence was noted for a reaction. When heated in an evacuated flask the SbCl_3 sublimed to cooler portion of the flask and no reaction occurred.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ with SOCl_2

Thionyl chloride^a (6.96 mmoles) was distilled into a 50 ml round bottom flask containing trimethylamine borane (0.51 mmoles). The reaction was warmed to -78° and after twenty minutes only a 1.5 mm increase in pressure occurred. On warming to -63° , after thirty minutes the pressure was 5.5 mm and after thirty minutes at -23° the pressure was 70.5 mm. The reaction was then warmed to 0° and after three hours the pressure was 126.0 mm. The reaction was condensed after an additional one hour and twenty minutes at room temperature (pressure 176.0 mm) and no non-condensable gas was present.

^aHCl impurity removed by distilling from -78° into -196° trap.

All the volatile material was transferred from the reaction flask, leaving a yellow residue. The infrared spectrum of the volatile reaction products implied mainly HCl (19). The material was fractionated by distilling from a -78° trap through a -119° trap into a -196° trap and infrared spectra obtained on each fraction. In the -196° trap only HCl (1.21 mmoles) was present, in the -119° trap mainly SO_2 (35) (0.331 mmoles) with a small amount of SOCl_2 was present, and in the -78° trap was SOCl_2 (25) with a slight impurity of SO_2 .

The flask increased in weight by 0.0985 g due to the reaction. A product was extracted from the yellow residue with boiling CCl_4 and the infrared spectrum of the material showed only $(\text{CH}_3)_3\text{NBHCl}_2$ to be present. An infrared spectrum on the CCl_4 insoluble yellow residue indicated that $(\text{CH}_3)_3\text{NHCl}$ was present as the principal infrared active material. There were peaks at 1200 cm^{-1} , 925 cm^{-1} and 550 cm^{-1} which could not be attributed to the amine hydrochloride. These could be due to SO or SCl bonds in another non-volatile and CCl_4 -insoluble reaction product.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and SO_2Cl_2

Trimethylamine borane (0.53 mmoles) was sublimed into a flask containing sulfuryl chloride (6.20 mmoles). The flask was warmed from -196° to -63° for thirty minutes and a

slow increase in the pressure occurred; on warming to -23° , the pressure initially increased rapidly and then increased steadily. After one hour the flask was warmed to 0° and no further increase in pressure occurred. On recondensing the flask in liquid N_2 , a small amount of non-condensable gas was present in the system.

All the volatile material was distilled from the flask, leaving a white residue. A gas phase infrared spectrum of the volatile material showed the presence of sulfuryl chloride (25), sulfur dioxide (35), and hydrogen chloride (19). An attempt to separate the HCl and SO_2 from the SO_2Cl_2 by distilling a fraction from -119° into a -196° gave quantitative separation of HCl from SO_2Cl_2 and SO_2 , and the infrared spectra indicated only HCl in the most volatile fraction. The gas phase spectra on the material remaining in the -119° trap was primarily that of SO_2 since SO_2 has a higher vapor pressure than SO_2Cl_2 .

The increase in weight of the reaction flask, if the product were pure $(CH_3)_3NBHCl_2$, implied a 97 per cent yield. The infrared spectrum of this material indeed was primarily that of $(CH_3)_3NBHCl_2$ but also indicated a trace of $(CH_3)_3NBHCl_2$ and some evidence for the $(CH_3)_3NH^+$ ion.

Reaction of $(CH_3)_3NBH_3$ and $ZnCl_2$ in glacial acetic acid

Trimethylamine borane (14.0 mmoles) was added to 50 ml of glacial acetic acid containing solid zinc chloride.^a

^aOn standing the zinc chloride dissolved in acetic acid.

The solution evolved gas vigorously. After ten minutes, approximately 75 ml of benzene was added to the solution and the mixture shaken before separating the two phases. The benzene phase was inadvertently lost. The acetic acid phase was neutralized with anhydrous K_2CO_3 and again extracted with benzene. The mixture was filtered and the benzene removed from the filtrate in a rotating evaporator leaving a clear film on the walls of the flask. This material was slurried with CCl_4 and stored in the freezer compartment of the refrigerator overnight. The next morning needle-shaped crystals were filtered from the cold CCl_4 solution. The infrared spectrum (Figure 29) of this material contained a BH_2 stretching vibration peak at $2360-2410\text{ cm}^{-1}$ and an intense absorption at 1690 cm^{-1} , possibly a carbonyl absorption. Qualitative test showed the compound contained boron, BH bonds, trimethylamine and no chloride. The material melted sharply at $58-60^\circ$ and was soluble in carbon tetrachloride, benzene and water. No change in the melting point occurred on recovering the compound from a water solution. Not enough material was recovered for a quantitative elemental analysis, but the data suggested that a possible formula of the material might be $(CH_3)_3NBH_2(O-\overset{O}{\parallel}C-CH_3)$. However, the experiment was not reproducible and the same

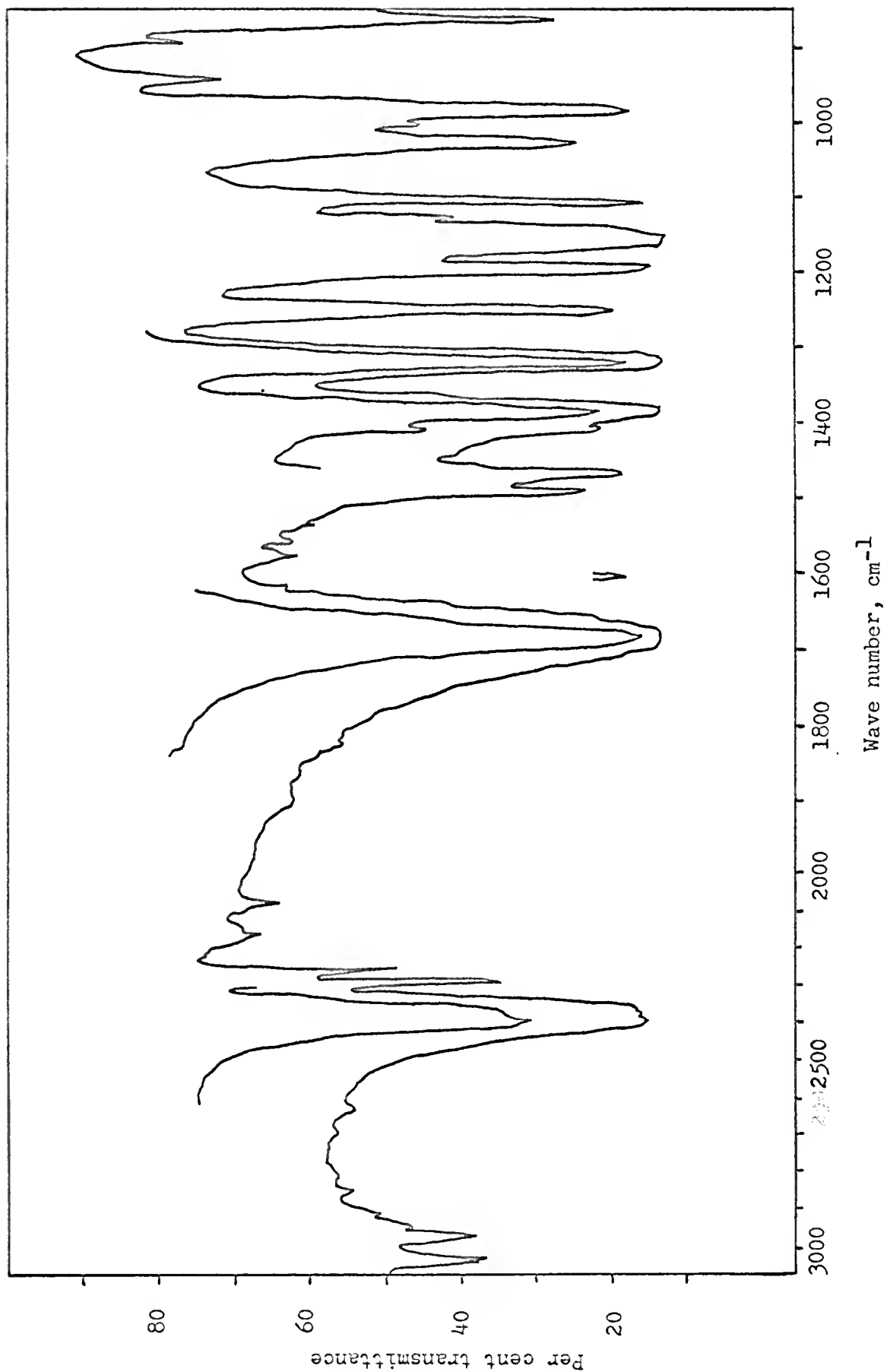


Fig. 29.---Infrared spectrum of the reaction product of $(\text{CH}_3)_3\text{NBH}_3$ and ZnCl_2 in glacial acetic acid.

material could not be prepared again. All attempts to do so failed.

Reactions of $(\text{CH}_3)_3\text{NBH}_3$ and $(\text{CH}_3)_3\text{NBCl}_3$ in an autoclave and the stability of the mono- and dichloroborane adducts under these conditions

Various ratios of trimethylamine borane and trimethylamine trichloroborane were heated in a stainless steel autoclave at 150° for nine to ten hours. A solid product was removed from the autoclave and recrystallized from hot CCl_4 . The results of the experiments are given in Table 20.

The infrared spectrum of the product produced by the reaction of one mole of $(\text{CH}_3)_3\text{NBH}_3$ with two moles of $(\text{CH}_3)_3\text{NBCl}_3$ was the only spectrum indicating a pure compound, $((\text{CH}_3)_3\text{NBHCl}_2)$. The melting point of this compound was $158-160^\circ$, and it was recovered in 90.6 per cent yield. A commercial analysis gave:

| Per Cent | C | H | N | Cl | B |
|---|-------|------|------|-------|------|
| Found | 25.17 | 6.93 | 9.86 | 50.27 | 7.87 |
| Calcd. for $(\text{CH}_3)_3\text{NBHCl}_2$ | 25.41 | 7.11 | 9.88 | 50.00 | 7.62 |

The tendency for $(\text{CH}_3)_3\text{NBHCl}_2$ to produce $(\text{CH}_3)_3\text{NBCl}_3$ when heated was greatly reduced when $(\text{CH}_3)_3\text{NBHCl}_2$ was heated in the presence of $(\text{CH}_3)_3\text{N}$ as may be seen in Figure 30. This implied that the $(\text{CH}_3)_3\text{N}$ was a possible intermediate in the reaction to produce $(\text{CH}_3)_3\text{NBCl}_3$.

TABLE 20

REACTION OF $(\text{CH}_3)_3\text{NBH}_3$ AND TRIMETHYLAMINE CHLOROBORANES ON HEATING

| Compound/mmoles | Reaction Time Hours | Reaction Temperature | Boron-Nitrogen Product |
|--|------------------------|----------------------|---|
| $(\text{CH}_3)_3\text{NBH}_3 + (\text{CH}_3)_3\text{NBHCl}_3$ | | | |
| 10.1 10.0 | 9.8 | 150° | $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ $(\text{CH}_3)_3\text{NBHCl}_2$ |
| 10.1 | 20.0 | 150° | $(\text{CH}_3)_3\text{NBHCl}_2$ |
| 20.0 | 9.98 | 150° | $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ $(\text{CH}_3)_3\text{NBHCl}_2^a$ |
| $(\text{CH}_3)_3\text{NBH}_2\text{Cl} + (\text{CH}_3)_3\text{NBHCl}_3$ | | | |
| 1.48 1.47 | 9.8 | 150° | $(\text{CH}_3)_3\text{NBHCl}_2$ $(\text{CH}_3)_3\text{NBHCl}_3^a$ |
| $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ | 24 | 185° | $(\text{CH}_3)_3\text{NBH}_2\text{Cl}, (\text{CH}_3)_3\text{NBHCl}_2$ |
| $(\text{CH}_3)_3\text{NBHCl}_2$ | 24 | 185° | $(\text{CH}_3)_3\text{NBHCl}_2, (\text{CH}_3)_3\text{NBHCl}_3$ |
| $(\text{CH}_3)_3\text{NBHCl}_2 + (\text{CH}_3)_3\text{NBHCl}_3$ | | | |
| 4.90 10.3 | 24 | 185° | $(\text{CH}_3)_3\text{NBHCl}_2, (\text{CH}_3)_3\text{NBHCl}_3^a$ |

^aOnly a small amount of the compound present.

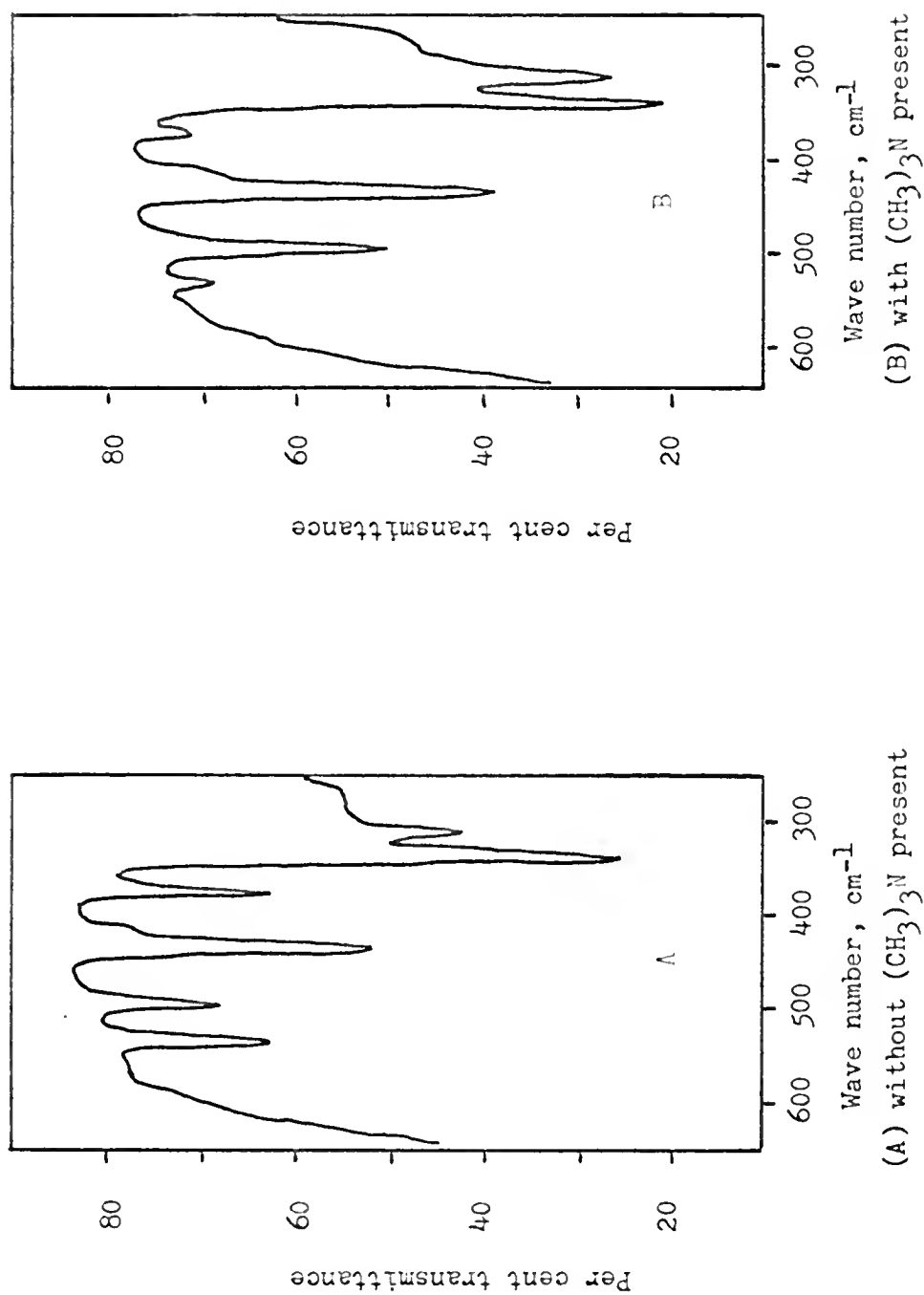


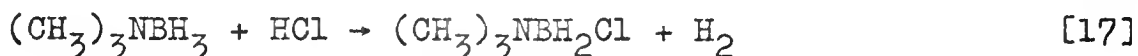
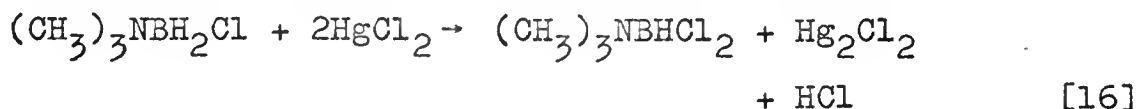
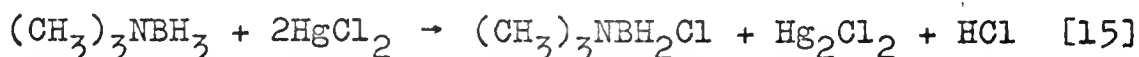
Fig. 30.--Comparison of product on heating $(\text{CH}_3)_3\text{NBHCl}_2$ with and without $(\text{CH}_3)_3\text{N}$ present.

DISCUSSION OF RESULTS AND CONCLUSIONS

Reactions of $(\text{CH}_3)_3\text{NBH}_3$ and HgCl_2

Trimethylamine borane reacted with mercuric chloride in diethyl ether to give the following products:

$(\text{CH}_3)_3\text{NBH}_2\text{Cl}$, $(\text{CH}_3)_3\text{NBHCl}_2$, Hg_2Cl_2 , HCl(g) and $\text{H}_2(\text{g})$, according to the following equations:



The products isolated from the reaction mixture depended upon the reaction time and method of addition of the HgCl_2 . In ether solution, the temperature did not affect which compounds were produced in the reaction. An infrared spectrum of the white solid material recovered from the ether solvent agreed with the superposition of the infrared spectra of pure $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and $(\text{CH}_3)_3\text{NBHCl}_2$. The ether solution was acidic to pH paper and had a strong odor of HCl . The white insoluble residue resulting from the reaction gave an x-ray diffraction pattern identical to that of a pure sample of reagent grade mercurous chloride. The non-condensable product (H_2) could be explained as a product

of the reaction between trimethylamine borane and the HCl produced by the reaction with HgCl_2 . It has been reported (40) that HCl will react with trimethylamine borane to give the monochloroborane adduct and H_2 gas. It has been confirmed in this laboratory that trimethylamine borane and HCl, in diethyl ether at 0° , formed the monochloro substituted adduct and hydrogen gas. This side reaction would account for the non-condensable product formed in the reaction. It would also account for the fact that slightly less than two moles of HgCl_2 were required per mole of BCl produced.

The equations were written in a stepwise sequence which was implied from the experimental observation that $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ reacted with HgCl_2 to give $(\text{CH}_3)_3\text{NBHCl}_2$. The next logical step did not occur in the ether solvent: $(\text{CH}_3)_2\text{NBHCl}_2$ did not react with HgCl_2 under these conditions.

The preparation of mono- or dichloro substituted amineboranes were not as clean-cut as the equations would tend to imply. If the reaction time was less than one hour or if the HgCl_2 was added as a solid to the trimethylamine borane-ether solution, the reaction would not give the products expected from the stoichiometric quantities. If the molar ratio was two moles HgCl_2 per mole of $(\text{CH}_3)_3\text{NBH}_3$, the products were primarily $(\text{CH}_3)_3\text{NBHCl}_2$ and a lesser amount

of $(\text{CH}_3)_3\text{NBHCl}_2$. If the ratio was four moles HgCl_2 per mole of $(\text{CH}_3)_3\text{NBH}_3$, or greater, the products were primarily $(\text{CH}_3)_3\text{NBHCl}_2$ and a lesser amount of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$. Even though excess $\text{HgCl}_2(\text{s})$ was added to the trimethylamine borane-ether solution and allowed to sit for several days, the reaction would not go completely to the dichloro adduct but some monochloro adduct would remain in the reaction mixture. It appeared as if the HgCl_2 became unreactive toward the trimethylamine borane.

An explanation for HgCl_2 becoming passive could be that the mercury metal in a very finely divided state, as it was produced in the redox reaction, reacted with the HgCl_2 on the surfaces of the crystalline HgCl_2 to form Hg_2Cl_2 . In this manner, the HgCl_2 crystals surfaces could become covered with unreactive, insoluble Hg_2Cl_2 , and thus prevent the crystal from dissolving or reacting further with the amineborane.

The reaction of $(\text{CH}_3)_3\text{NBH}_3$ with HgCl_2 could be made to go completely to the dichloro adduct. If the HgCl_2 was dissolved from a Soxhlet extractor filter thimble by refluxing ether and added, in this manner, to a trimethylamine borane-ether solution, the reaction would go completely to the dichloroborane trimethylamine adduct. In this case, the HgCl_2 was added as a homogeneous solution to a solution of trimethylamine borane. The time required for the addition

of HgCl_2 to the $(\text{CH}_3)_3\text{NBH}_3$ was limited by the solubility of the HgCl_2 in diethyl ether. The reaction was complete at the dichloro product and further refluxing of the reaction mixture did not cause the reaction to proceed further even though Hg(II) was present. Therefore, this was found to be a good method to prepare useful quantities of $(\text{CH}_3)_3\text{NBHCl}_2$.

Trimethylamine dichloroborane was characterized for the first time in this work. Schlesinger, Flodin and Burg (40) had claimed this compound as the result of long-term heating at 100° of HCl(g) and $(\text{CH}_3)_3\text{NBH}_3$, but they gave no experimental details or properties of the compound. In this work, the compound was found to be a white solid having a melting point in the range of $145\text{--}150^\circ$. The infrared spectrum is given in Figure 23 and the NMR spectrum in Figure 26.

The reaction of trimethylamineborane with two moles of HgCl_2 to prepare $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ did not give a pure product. Invariably, the isolated product was a mixture of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and $(\text{CH}_3)_3\text{NBHCl}_2$. The material was primarily the mono substituted product, but it could not be made the sole product of the reaction. The side reaction of $(\text{CH}_3)_3\text{NBH}_3$ and HCl increased the yield of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and at the same time reduced the amount of HgCl_2 necessary to produce only the $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$. The difficulty (or im-

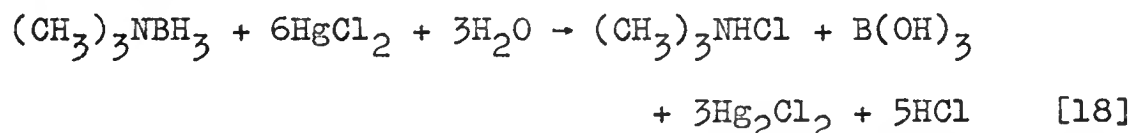
practicality) of separating the $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and $(\text{CH}_3)_3\text{NBHCl}_2$ made this method unattractive as a means to prepare $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$.

Experimentally it was observed that in ether solution the HgCl_2 did not discriminate to any detectable extent in reacting with $(\text{CH}_3)_3\text{NBH}_3$ and $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$, but it did discriminate in reacting with $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and $(\text{CH}_3)_3\text{NBHCl}_2$. Mercuric chloride reacted with $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ but did not react with $(\text{CH}_3)_3\text{NBHCl}_2$ in refluxing ether. Thus, mercuric chloride reacted to substitute two chlorine atoms for hydrogen atoms on the boron atom in trimethylamine borane, but would not substitute the third chlorine atom for the last hydrogen atom on the boron atom in diethyl ether. However, under appropriate conditions, all three BH bonds can be reacted with excess HgCl_2 to give $(\text{CH}_3)_3\text{NBCl}_3$. When $(\text{CH}_3)_3\text{NBH}_3$ and excess HgCl_2 were heated in an autoclave for nine hours at 100° , the reaction did not go to completion but it did produce a substantial amount of $(\text{CH}_3)_3\text{NBCl}_3$ in addition to the other two chloro substituted adducts. In this reaction, the Hg(II) reacted to form mercury metal instead of the usually recovered Hg_2Cl_2 product. Thus, the BH bond in $(\text{CH}_3)_3\text{NBHCl}_2$ required more energetic conditions to react.

Trimethylamine borane reacted with mercuric chloride in a water solution to give approximately 2 per cent yield

of the monochloro adduct, but the primary product of the reaction was boric acid and hydrochloric acid.¹ A high concentration of chloride ion in the water solution did not affect the recovered products of the reaction to any significant extent, but the reaction was slower in the chloride solution than in water solution. The solubilities of the reactants appeared to be different in the chloride solution, the amine borane less soluble and the mercuric chloride more soluble. The enhanced solubility of mercuric chloride could be explained by the formation of tetrachloromercurate(II) ion in the chloride solution and the decreased rate of reaction, by the tetrachloromercurate(II) ion being less reactive toward the BH bond than toward the uncomplexed mercury(II) ion.

The change in pH during the reaction of $(\text{CH}_3)_3\text{NBH}_3$ and HgCl_2 in water indicated that the reaction was essentially complete within six seconds. The change in pH and the amount of strong acid produced implied that the reaction had proceeded according to the following equation:



Thus, the reaction to produce $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ must have been a side reaction, or the $(\text{CH}_3)_3\text{NBHCl}_2$, if produced from $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ must have hydrolyzed immediately.

The rate of change in pH during the reaction of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and HgCl_2 in water implied that the reaction was slower than the reaction with $(\text{CH}_3)_3\text{NBH}_3$. The pH of $(\text{CH}_3)_3\text{NBHCl}_2$ slurried with a water-ethanol mixture (20:1) decreased slowly at a steady rate, and the addition of HgCl_2 did not affect the rate of decrease in the pH. Therefore, Hg(II) ion did not react with the BH bond in $(\text{CH}_3)_3\text{NBHCl}_2$ in water solution to any measurable extent.

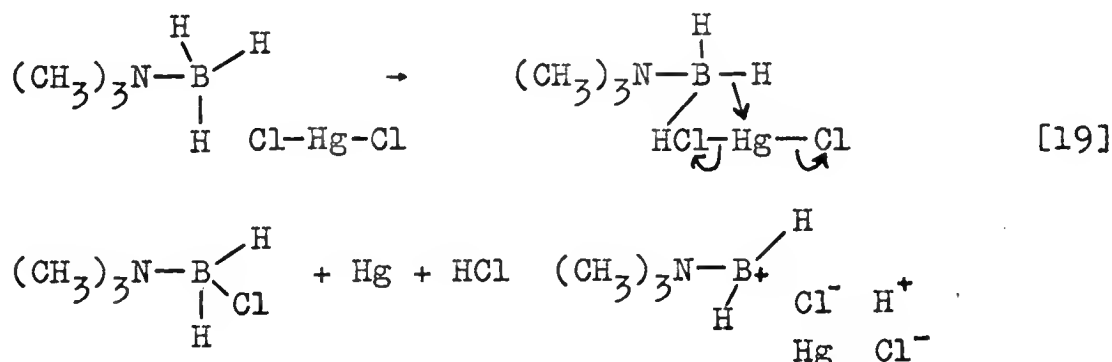
This suggested that the initial reaction between a BH bond and Hg(II) ion resulted in the formation of boric acid and not in the formation of a BCl bond, which then underwent hydrolysis. Since the reaction rate of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ with HgCl_2 was slow, if $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ had been a product or intermediate in the reaction of $(\text{CH}_3)_3\text{NBH}_3$ and HgCl_2 in water the pH change curve should have had a point where the rate of change in pH decreased since the reaction rate of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ with HgCl_2 was slow. This break point would have corresponded to a build up of the $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$. But, since no change in the rate of decrease of the pH occurred when $(\text{CH}_3)_3\text{NBH}_3$ reacted with HgCl_2 in water, it may be concluded that no significant amounts of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ were produced as an intermediate in the reaction, but that the reaction produced boric acid and HCl as the primary products.

The reaction between the BH bond and the Hg(II) ion may be considered to be an oxidation-reduction reaction

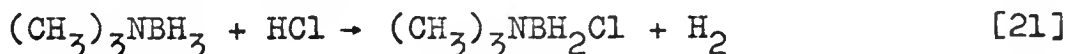
with the BH bond as the reducing agent and the Hg(II) ion the oxidizing agent. Considering the experimental results, a plausible mechanism would be one in which a two-electron transfer step occurred.

The Hg(II) ion was attracted to the electronic density of the BH bond and accepted two electrons from the bond. This would give mercury metal, H^+ , and any intermediate $[(CH_3)_3NBH_2^+]$. The positive site on the boron attracts a base (X^-) to give $(CH_3)_3NBH_2X$. This process most likely occurred in one step. The activated complex would most probably be one in which Hg(II) accepted the electrons from the BH bond as the Cl^- approached and the H^+ left, rather than a stepwise process involving complete ionization.

The mechanism may be graphically depicted by the following sequence of configurations:



Subsequent reactions:



This is essentially a similar mechanism to the one suggested by Hawthorne (17) for the hydrolysis of a pyridine diphenyl borane and to the one proposed as a mechanism for the reaction of dimethylamine borane to eliminate hydrogen in Part I of the dissertation. The intermediate $(\text{CH}_3)_3\text{NBH}_2^+$ would be expected to be very reactive. Three-coordinate boron species are usually reactive due to the empty orbital and a three coordinate boron species having a positive charge would be expected to be even more reactive. The expected reactivity would argue against a stepwise process. The mercury metal reacted with the Hg(II) in the system to give Hg(I) which could precipitate as the insoluble salt. Mercury metal was a reaction product in the autoclave reactions where no solvent was used and the Hg(o) and Hg(II) did not have as good an opportunity to come in contact. The H^+ reacted with the hydridic BH hydrogen to give H_2 and another boron intermediate which immediately reacted with a base to give $(\text{CH}_3)_3\text{NBH}_2\text{X}$. Thus, the mechanism accounts for all the observed products.

If an electron transfer step was proposed where the Hg(II) accepted only one electron from the hydridic BH bond, the hydrogen retained the other electron, and leaving the boron with an acceptor site, this would account for the Hg_2Cl_2 , but it would also give hydrogen atoms which would require that H_2 be a major reaction product, which it was

not. It would not account for the HCl or mercury metal observed in the reactions and would be contrary to the observed data.

The proposed activated complex for the mechanism implied that the compound bonded to the boron atom after reaction must be the same component as originally present in the primary coordination sphere of the Hg(II) ion. The experimental results were consistent with such a configuration for the activated complex. In ether solution, the HgCl_2 would be present primarily as the molecular species and the chlorine atoms would be close to the mercury atoms. In the solid phase reactions the chlorine atoms would be closest to the mercury atoms, and in both cases the observed reaction products were the chloroborane adducts. In water solution, the mercury(II) ion would be surrounded by solvent molecules and in the activated complex it would be a water molecule instead of a chloride ion which would be forming a bond to the boron atom. The resulting species would be expected to hydrolyze immediately. The small amount of monochloro adduct recovered from the water solution could result from Hg(II) ions which still had a chloride ion remaining in the primary coordination sphere. The failure to increase the amount of monochloro adduct produced by increasing the concentration of chloride ion in the solvent and the apparent decreased reaction rate implied a difference in the

reactivity toward the BH bond of a simple Hg(II) ion and the tetrachlormercurate(II) ion.

Thus, the proposed mechanism, where Hg(II) ion accepted two electrons, explained and was consistent with all the observed experimental results for the reaction of trimethylamine borane and mercuric chloride.

The side reaction between the unreacted trimethylamine borane and the hydrogen chloride produced by the reaction with Hg(II) raised the question as to which reagent reacted faster with trimethylamine borane. Mercuric chloride reacted faster than HCl with $(\text{CH}_3)_3\text{NBH}_3$ at 0° in diethylether. An ether solution of $(\text{CH}_3)_3\text{NBH}_3$ was poured into an ether solution of HCl and HgCl_2 . The molar ratio of reactants was $1(\text{CH}_3)_3\text{NBH}_3 : 1\text{HCl} : 2\text{HgCl}_2$. The H_2 produced was found to be approximately twenty mole per cent of the hydrogen which could have been produced by complete reaction of the HCl with the amineborane. The reaction time was sufficiently long so that the HgCl_2 would have reacted completely with the trimethylamine borane, if no HCl had been present. This means that 80 per cent of the trimethylamine borane reacted with the HgCl_2 . The HgCl_2 was not completely dissolved in the ether, but a small portion of the solid was suspended in the solvent. The HCl was in solution and each time a HgCl_2 molecule reacted, it produced one of HCl. Therefore, the HCl should have had the advantage of being in more

homogeneous contact with the trimethylamine borane and of being replenished by the competing reaction. The HgCl_2 reaction being faster than the HCl reaction agreed with the qualitative observations. An ether-trimethylamine borane solution and a HgCl_2 -ether solution, when mixed, gave an immediate white precipitate. This precipitation appeared to be complete within a few minutes and no further visible changes in the system were noticeable.

Nevertheless, the reaction of HCl(g) with trimethylamine borane, in ether at 0° or benzene at 25° , was a good method to prepare useful quantities of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$. The reaction was complete at the monosubstituted adduct under these conditions. To prepare the dichloro adduct from these reagents it was necessary to heat the two compounds in an autoclave at 100° for twenty-four hours. This had been reported (40) previously and was confirmed in this laboratory.

A report in the patent literature by Borer and Dewing (2) of the preparation of the monochloro adduct from trimethylamine borane and concentrated hydrochloric acid was investigated and found to be correct. In the preparation procedure reported (2), it would have been possible for the monochloro adduct to have been formed during the benzene extraction by a reaction of amine borane and HCl , which would both be extracted into the benzene phase. Borer and

Dewing's procedure was repeated except that the water solution was neutralized with NaOH solution before extraction with benzene; a small amount of the monochloro adduct was still recovered from the benzene extraction phase.

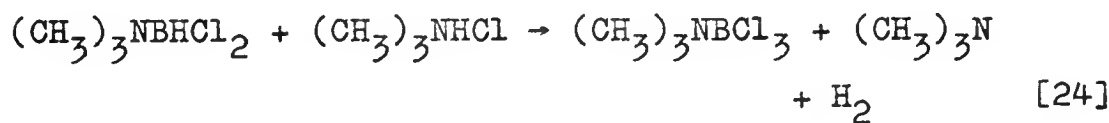
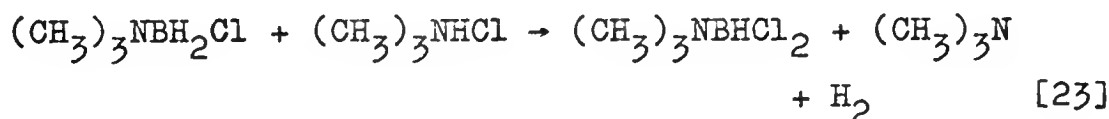
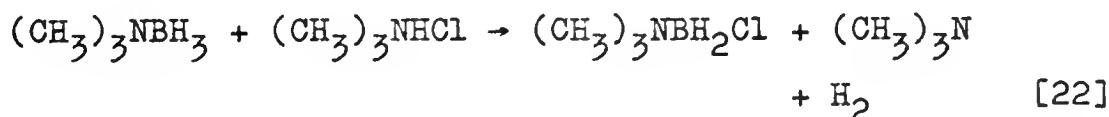
Thus, the monochloro adduct was formed in the concentrated hydrochloric acid. The monochloro adduct was prepared, using concentrated HCl(aq) as a source of HCl, by adding the concentrated acid to a benzene solution of trimethylamine borane. After shaking, the water-benzene phases were separated and the HCl which extracted into the benzene reacted with the amine borane. The monochloro adduct could be recovered in approximately 45 per cent yield but the infrared spectra implied that the reaction was not quite completed in forty-five minutes. Other organic solvents, e.g., CCl_4 , could be used for this reaction procedure.

The reaction mechanism for the reaction of a BH bond with HCl would be one in which H^+ acted as the oxidizing agent, accepting electrons from the BH bond to form hydrogen gas. This is the same mechanism as has been previously suggested for the Hg(II) reaction. The mechanism is consistent with the observed experimental results.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and $(\text{CH}_3)_3\text{NHCl}$

Trimethylamine borane reacted with trimethylamine hydrochloride to give the chloro-substituted adducts. On

heating the solid reagents to 150-185° for fifty hours, mono- and dichloro adducts were isolated. In order to get a more complete reaction, it was necessary to remove the trimethylamine product about halfway through the reaction time and then reheat the mixture. The reaction products implied that the following reactions occurred.

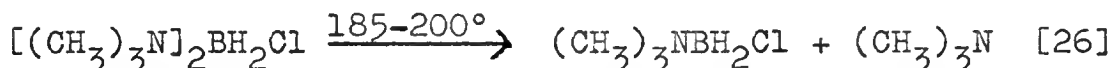
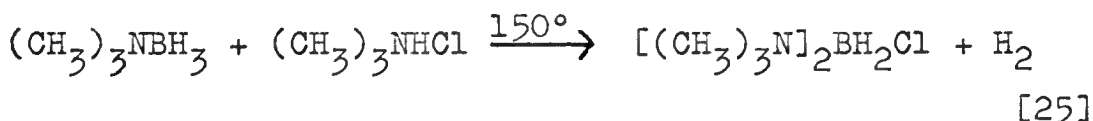


If the starting materials for the reaction were $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ and $(\text{CH}_3)_3\text{NHCl}$, equation [23], then the reaction product contained the trichloro adduct. The trichloro adduct was not obtained in any of the experiments where the starting reagent was trimethylamine borane. But, the products recovered were strongly affected by the trimethylamine produced in the reaction. The compounds were not very stable at these high temperatures (150-185°) for extended periods of time (24-50 hours) and the products were recovered only in small yields (~ 40 per cent); usually contaminated with the amine hydrochloride. However, the initial preparation of pure trimethylamine dichloroborane was accomplished by this method. Considering the

reaction products and their dependence on the presence of trimethylamine the following mechanism was proposed.

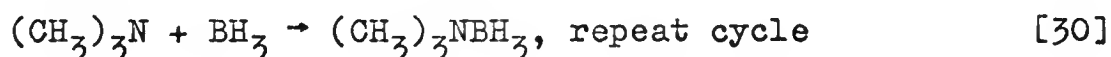
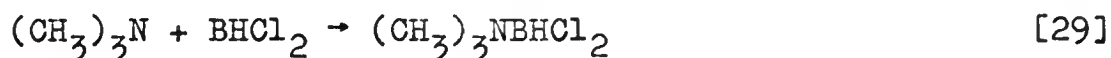
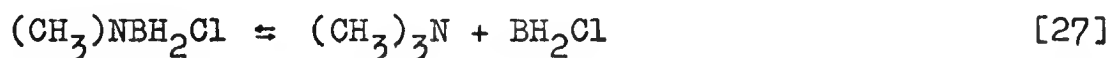
The protonic hydrogen in the trimethylammonium ion accepted an electron pair from the hydridic hydrogen in the BH bond to produce hydrogen, trimethylamine, and an acceptor site on the boron atom. A competition for the site on the boron occurred between trimethylamine and the chloride ion, and the experimental conditions determined which was the stronger base toward the boron atom.

Miller, Chamberland, and Muetterties (26) have reported that the following reactions occur:



Therefore, the evidence suggested that at lower temperatures the trimethylamine was the stronger base, forming a boronium ion, and at higher temperatures the chloride ion was the stronger base. The mechanism was the same except the trimethylammonium ion attacked the BH bond. There were two possible mechanisms which could account for the second (or third) step of the reaction sequence. The first, and most probable one, would be a repetition of the first step with the chloride ion being the stronger base toward boron than the trimethylamine, under the experimental conditions. The

second would be a dissociation of the amine monochloroborane into the amine and monochloroborane, followed by a disproportionation of the monochloroborane into borane and dichloroborane which then recombined with the amine to form trimethylamine dichloroborane according to the following equations:

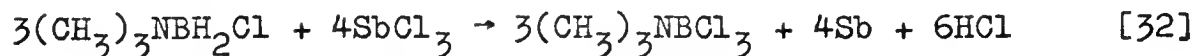
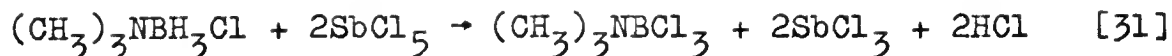


Diborane and trichloroborane have been reported (5) to disproportionate and the various chloroboranes have been trapped as the diethyletherates. In our experiments a sample of $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ after heating at 185° for twenty-four hours was found to contain some $(\text{CH}_3)_3\text{NBHCl}_2$.

Both mechanisms account for the experimental results and neither can be completely discounted.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and SbCl_5

Antimony pentachloride reacted violently with trimethylamine monochloroborane to form an acidic gas (HCl), $(\text{CH}_3)_3\text{NBCl}_3$, SbCl_3 , and a grey powdery material (Sb). The following equations were suggested by the data:



The antimony trichloride produced in the reaction did not react with the BH bond in ether solution but as soon as the ether was removed a reaction occurred slowly to produce a grey material. Thus, the etherate of antimony trichloride stabilized the antimony (III) toward further reaction with the BH bond.

The dichloroborane adduct also reacted vigorously with SbCl_5 to produce the grey powder and a gas. The grey reaction product occurred in each of the reactions, and visually appeared to be a metallic powder. The powder was oxidized in nitric acid, the solution buffered with ammonium acetate, and the orange-red antimony oxysulfide complex formed on the addition of $\text{Na}_2\text{S}_2\text{O}_3$ crystals proving the powder to contain antimony, but not what oxidation state it was originally.

A similar mechanism could be proposed for the reactions of SbCl_5 and SbCl_3 as was given for the reaction of Hg(II) ion in which the metal atom accepted electrons from the BH bond.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and SbCl_3

Qualitative reactions between antimony trichloride and trimethylamine borane and the chloroboranes confirmed

the fact that they react to give a grey-black residue which, in the case of the trimethylamine borane reaction, resulted in a metallic mirror covering the flask. The metallic mirror indicated that the grey-black material was indeed metallic antimony.

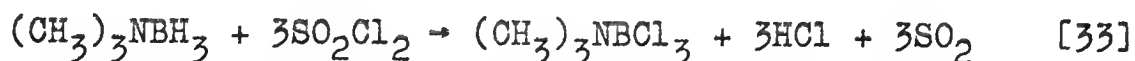
The experiments showed that the order of reactivity of the amine boranes with SbCl_3 was $-\text{BH}_3 > -\text{BH}_2\text{Cl} > -\text{BHCl}_2$. Antimony trichloride and $(\text{CH}_3)_3\text{NBHCl}_2$ formed a clear liquid when the solids came into contact which slowly turned dark. The infrared spectrum in the range of $4000\text{--}600\text{ cm}^{-1}$ indicated no change in the spectrum of the starting material other than perhaps some formation of $(\text{CH}_3)_3\text{NBCl}_3$. No explanation other than the formation of a low melting eutectic mixture of the solid materials seemed reasonable unless some sort of liquid polymeric species was formed in which the boron bonded chlorines were acting as a Lewis acid and the SbCl_3 acting as a Lewis base. But no reaction occurred between $(\text{CH}_3)_3\text{NBCl}_3$ and SbCl_3 which could be reasonably expected if the SbCl_3 acted as a Lewis acid to accept an electron pair from a chlorine bonded to boron to form a liquid polymeric species containing chlorine bridges.

Thus far, the oxidizing agents used here to react with the BH bond have been either a high oxidation state metal, that is, Hg(II) , Sb(V) , Sb(III) or a protonic species. Compounds of non-metallic elements in high oxidation states,

that is, P(V), S(VI), S(IV), should undergo analogous reactions; and therefore, the reactions of sulfuryl and thionyl chloride with the amine borane were considered.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and SO_2Cl_2

Sulfuryl chloride reacted with trimethylamine borane in a straight-forward manner according to the equation:

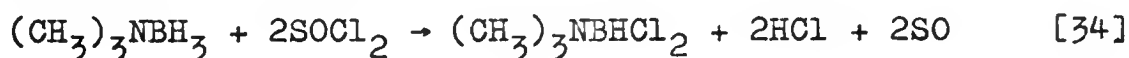


The reaction occurred on warming slowly from -78° to -23° . The weight increase during reaction implied 97 per cent yield of $(\text{CH}_3)_3\text{NBCl}_3$, but the infrared spectrum implied a small impurity of $(\text{CH}_3)_3\text{NBHCl}_2$. Each of the products was identified by its infrared spectrum; HCl (1.50 mmoles) was separated from the SO_2 and SO_2Cl_2 , but the other two components could not be separated.

The same electron transfer mechanism as previously outlined was also proposed for this reaction. The sulfur atom accepted two electrons forming the stable SO_2 molecule which was given off as a gaseous product just as the Hg(II), Sb(V) and Sb(III) have been proposed to accept electrons to form stable species of a lower oxidation state. The evidence for a small amount $(\text{CH}_3)_3\text{NBHCl}_2$ in the solid reaction products' infrared spectrum of $(\text{CH}_3)_3\text{NBCl}_3$ suggested that the formation of the trichloro adduct also occurred in steps.

Reaction of $(\text{CH}_3)_3\text{NBH}_3$ and SOCl_2

Thionyl chloride reacted with trimethylamine borane to form the dichloroborane adduct, HCl , SO_2 , and a sulfur containing residue. Considering the reaction to be analogous to the reaction with sulfuryl chloride, the following equations may be written.



The intermediate compound SO which was proposed by these equations has not been reported as a stable species, but was suggested by analogy.

The reaction occurred very slowly at -63° , slightly faster at -23° and at a convenient rate at 0° . The gaseous products were separated and infrared spectra confirmed their identity. The solid reaction residue was separated into $(\text{CH}_3)_3\text{NBHCl}_2$ and a yellow residue and the infrared spectra obtained confirmed the dichloro adduct. The spectrum of the yellow residue contained $(\text{CH}_3)_3\text{NHCl}$ as the major infrared active component but it also showed an intense peak at 1200 cm^{-1} and less intense peaks at 925 cm^{-1} and 550 cm^{-1} . The stoichiometry of equation [34] was not confirmed by the measured amounts of HCl and SO_2 gas. More HCl(g) (1.21 mmoles compared to 1.01 mmoles) was recovered than would be implied by equation [34] and less SO_2 (0.33 mmoles compared to 1.01 mmoles) was recovered. The weight

of non-volatile products of the reaction was also larger (0.98g) than would be predicted by equation [34] (0.0880g). Thus, equation [34] as written does not describe completely the stoichiometry of the actual reaction.

The proposed mechanism would be the same electron transfer process as previously suggested with the sulfur atom accepting the electrons followed by a decomposition of the reduced sulfur containing species. This was the same mechanism as in the previous cases except that the reduced sulfur compound in this instance was not a stable compound.

Conclusions from the reactions

Each of the reactions discussed so far may be considered, and have been considered, as an oxidation-reduction reaction with the BH bond as the reducing agent and a variety of different oxidizing agents. Each reaction involving the BH bonds was found to be a stepwise reaction and the number of BH bonds reacted per molecule varied with the oxidizing agent or with the experimental conditions. Hydrogen chloride reacted with trimethylamine borane to give the monochloro adduct at room temperature, mercuric chloride gave the dichloro adduct, and antimony pentachloride gave the trichloro adduct under the same conditions thus implying an ordering in the relative strength of the oxidizing agents toward the BH bond in the amine borane and indicating a

change in the BH bonds' reactivity during the reaction. For the reagents which gave a product which still contained a BH bond, the reaction occurred to a further extent if the conditions were made more energetic. This showed that the reducing ability of a BH bond decreases as chlorine atoms were substituted for hydrogen atoms.

The work of Noeth and Beyer (32) was also consistent with a change in reactivity of the BH bond as the substituents bonded to boron changed. They reported that trimethylamine borane reacted with HBr, HI and I_2 to give the mono-substituted adduct and that chlorine, bromine, and HF reacted with the amine borane to give the tri-substituted adducts.

The decrease in reactivity of the BH bond as a reducing agent on chloro substitution may be explained in the following manner.

Once the more electronegative chlorine atom is bonded to the boron atom, it would tend to shift the electron density in the bond more toward the chlorine. This in turn would cause a shift toward the boron of the electron density in the remaining BH bonds, the net result being that the attached hydrogens were less hydridic and would therefore be weaker reducing sites. A second chlorine bonded to the boron would make the remaining BH bond even less hydridic and, by this argument, it would not be expected to be a very

strong reducing agent. This should also cause a strengthening of the BN bond, but this would be countered by increased steric strain due to the size of the chlorine atoms.

Essentially, this same inductive argument has been used by Muetterties (28) to explain the reduced reactivity of BH bonds in the boronium ions.

The inductive effect argument was confirmed by the B^{11} chemical shifts observed in the nuclear magnetic resonance spectra of the amine borane and chloroborane compounds. The chemical shift, which may be considered as a measure of the electronic density about the nucleus, suggested that the order of electronic density about the boron atom decreases in the following manner, $(CH_3)_3NBH_3 > (CH_3)_3NBH_2Cl > (CH_3)_3NBHCl_2 > (CH_3)_3NBCl_3$. Thus the hydridic character of the BH bond should decrease in the same order as the electronic density on the boron atom. The largest change in the chemical shifts occurred between the monochloro and dichloro-substituted adducts and it was between these two compounds that the greatest change in the reactivity of the BH bond was noted.

From the experimental conditions and from the extent of reaction it was possible to predict an ordering of the strength of the oxidizing agents toward the BH bond. The experimentally observed order of reactivity was $SbCl_5 > SO_2Cl_2 > SOCl_2 > HgCl_2 > HCl > (CH_3)_3NHCl$. Antimony

trichloride was not included because a quantitative experiment using it as the oxidizing agent was not attempted, but the qualitative indications implied that it would probably be intermediate between sulfuryl and thionyl chloride. The ordering was based primarily on the following considerations:

1. SbCl_5 reacted to give only $(\text{CH}_3)_3\text{NBCl}_3$.
2. SO_2Cl_2 reacted to give $(\text{CH}_3)_3\text{NBCl}_3$ but also some $(\text{CH}_3)_3\text{NBHCl}_2$ remained in the system.
3. SOCl_2 reacted to give $(\text{CH}_3)_3\text{NBHCl}_2$ below 0° .
4. HgCl_2 reacted at 0° to give $(\text{CH}_3)_3\text{NBHCl}_2$.
5. HCl reacted at room temperature to give $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$.
6. $(\text{CH}_3)_3\text{NHCl}$ reacted only at elevated temperatures.

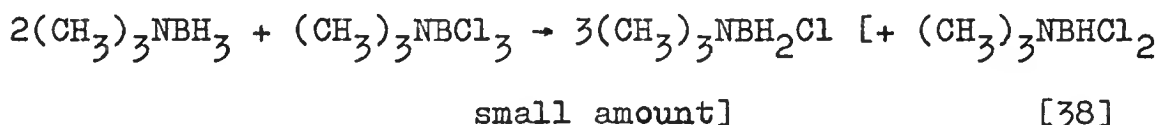
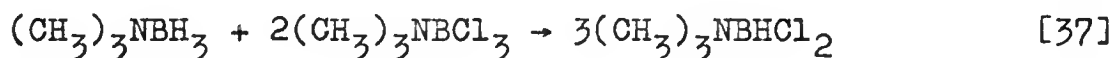
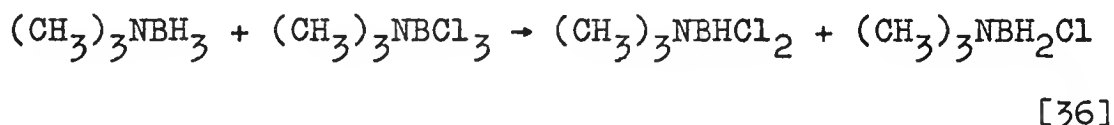
Thus, from these considerations it would be possible to pick the oxidizing agent to give the best preparation of a desired product.

Thermal stability of the adducts

The thermal stability toward disproportionation of trimethylamine borane and the chloroboranes could determine which products were recovered from an experiment involving high temperatures for long periods of time. Therefore, a preliminary study was made of the stability of these adducts toward interconversion of one adduct into another.

Trimethylamine borane and trimethylamine trichloroborane, in a 1:1 molar ratio, were heated for nine to ten

hours at 150° in an autoclave; the recovered product was found to contain the mono and dichloro adducts with no evidence for the presence of the starting materials in the infrared spectrum. If the stoichiometry were varied to two moles of trimethylamine trichloroborane to one mole of trimethylamine borane, the recovered product was trimethylamine dichloroborane. But if the stoichiometry were the reverse of that, namely, two moles amine borane to one mole amine trichloroborane, the recovered product was the monochloro adduct; a small amount of the dichloro adduct was evident in the infrared spectrum. The reactions may be summarized in the following equations:



The results suggested that the dichloro adduct was the most stable one under these conditions. This idea was further supported by the heating of the monochloro adduct alone and finding evidence for the dichloro adduct in the recovered material.

The monochloro and trichloro adducts when heated under the same conditions gave primarily the dichloro adduct with

a small amount of the trichloro adduct in the recovered material. The results implied that there was an extra stability associated with the dichloroborane adduct which the other adducts did not have. Ratajaczak (36) reported that triethylamine dichloroborane appeared to have some special stability and that when one mole of $(C_2H_5)_3NBH_3$ reacted with more than one mole of $BCl_3(g)$ only $(C_2H_5)_3NBHCl_2$ was isolated.

The dichloro adduct when heated for twenty-four hours at 185° gave as recovered products the starting material and the trichloro adduct. But, when heated in the presence of trimethylamine the recovered product was greater in yield and was principally the dichloro adduct with only a small amount of the trichloro adduct present. The trimethylamine thus suppressed the reaction.

In view of the experimental results, the following mechanism was proposed for the rearrangement reactions of the borane adducts. The first step would be a dissociation of the amine borane into the amine and the borane, the second step would be a disproportionation reaction of the boranes, and the third step would be a recombination of the borane and amine. The effect of trimethylamine on the tendency of the dichloroborane adduct to undergo disproportionation indicated that the mechanism involved trimethylamine. Thus, a dissociation of the amine borane occurred

during the reaction. This is the same mechanism presented as a possibility for the second step in the reaction of $(\text{CH}_3)_3\text{NBH}_3$ and $(\text{CH}_3)_3\text{NHCl}$.

Therefore, it may be concluded that the recovered products from an experiment using high temperature for extended periods of time may or may not be the primary reaction product but may have been produced by subsequent disproportionation reactions.

SUMMARY

Trimethylamine chloroboranes were prepared by reacting trimethylamine borane, $(\text{CH}_3)_3\text{NBH}_3$, with mercuric chloride, hydrogen chloride, trimethylamine hydrochloride, antimony pentachloride, antimony trichloride, sulfuryl chloride, thionyl chloride, and trimethylamine trichloroborane $(\text{CH}_3)_3\text{NBHCl}_3$. The extent of chloro substitution on the borane was a function of which reagent was used and the reaction conditions.

Trimethylamine dichloroborane, $(\text{CH}_3)_3\text{NBHCl}_2$, was prepared and it was characterized for the first time in this work.

The reactions were all considered to be oxidation-reduction reactions in which the BH bond was the reducing agent. An order of reactivity of the oxidizing agents was determined to be: $\text{SbCl}_5 > \text{SO}_2\text{Cl}_2 > \text{SOCl}_2 > \text{HgCl}_2 > \text{HCl} > (\text{CH}_3)_3\text{NHCl}$.

The reactivity of the BH bond decreased on chloro substitution of the boron atom in the order: $-\text{BH}_3 > -\text{BH}_2\text{Cl} > -\text{BHCl}_2$.

This decrease in reducing ability of the BH bond was explained by an inductive effect in which the chlorine atoms

withdrew electronic density from the boron atom, and thus from the BH bond. The model was consistent with the B¹¹ nuclear magnetic resonance spectra of the compounds.

A mechanism was proposed in which the oxidizing agent accepted an electron pair from the hydridic BH bond. The mechanism proposed a non-linear activated complex and was similar to the mechanism proposed by Hawthorne (17) for hydride transfer reactions. The mechanism was consistent with all the experimental results.

The basic idea of using the reactivity of the BH bond as a means to prepare B-substituted amine boranes appeared to be one worthy of further investigation.

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BIOGRAPHICAL SKETCH

James William Wiggins was born March 5, 1940, at Paris, Arkansas. In May, 1958, he was graduated from Paris High School. In June, 1962, he received the degree of Bachelor of Science from the University of Arkansas. In September, 1962, he enrolled in the Graduate School of the University of Florida. He worked as a teaching assistant and a graduate assistant while pursuing his work toward the degree of Doctor of Philosophy. From September, 1964 until June, 1965, he was the DuPont Post Graduate Teaching Fellow.

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 17, 1966

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